



Figure 3.—Optical spectrum of Delépine's (III, IV, IV) salt in concentrated  $\text{H}_2\text{SO}_4$ .

pine's salt. However, unlike Lecoq's salt, the Delépine salt shows no absorption in the 9000–15,000-Å region. Within the framework of the mixed-valence theory,<sup>2</sup> the lack of mixed-valence absorption in Delépine's salt could be taken as the result of a very firm trapping of the valences and a tendency toward class I behavior.

This arises from substantially different ligand fields at the metal atoms of different valence. The preliminary Mössbauer results are also consistent with the idea of Lecoq's (III, III, IV) salt being more class II than Delépine's (III, IV, IV) salt.

Though our experiments directed toward uncovering the structures of these complexes are far less direct than a crystal structure analysis (presently in progress), they do uncover the gross features of the structures. First, all oxidation states of the Lecoq and Delépine salts are trimeric. The ligand fields about the metal atoms of formally different valence are sufficiently different in the mixed-valence ions that the integral valences may be considered as trapped, in the lowest approximation. However, sufficient delocalization of the valences is present to pair all electron spins, except in odd electron species. The close parallel in the properties of the Lecoq and Delépine systems demonstrates that they have very similar structures.

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## The Heat Capacity of Potassium Perbromate, $\text{KBrO}_4$ , between 5 and 350°K<sup>1</sup>

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The heat capacity of crystalline potassium perbromate has been measured by an adiabatic technique between 5 and 350°K. The standard entropy, enthalpy increment, and Gibbs energy function have been calculated as functions of the temperature. At 298.15°K these functions have the respective values  $S^\circ = 170.09 \pm 0.17 \text{ J deg}^{-1} \text{ mol}^{-1}$ ,  $H^\circ - H^\circ_0 = 23,400 \pm 24 \text{ J mol}^{-1}$ , and  $-(G^\circ - H^\circ_0)/T = 91.605 \pm 0.092 \text{ J deg}^{-1} \text{ mol}^{-1}$ , and  $C_p^\circ$  is  $120.17 \pm 0.12 \text{ J deg}^{-1} \text{ mol}^{-1}$ . The standard Gibbs energy of formation from the elements at 298.15°K has the value  $\Delta G_f^\circ = -174.1 \pm 0.6 \text{ kJ mol}^{-1}$ . In aqueous solution at 298.15°K the standard entropy of the perbromate ion has the value  $S^\circ = 199.8 \pm 1.6 \text{ J deg}^{-1} \text{ mol}^{-1}$  on the conventional scale with  $S^\circ(\text{H}^+, \text{aq}) = 0$ . The standard entropies of all the halate and perhalate ions are compared, and comments are made on the exceptionally low entropy of the iodate ion,  $\text{IO}_3^-$ .

### Introduction

With the synthesis of perbromates a problem was solved that had been puzzling inorganic chemists for a long time. Although both chlorine and iodine are readily oxidizable to the highest valence state expected for elements of the seventh group, all attempts to produce compounds of heptavalent bromine remained unsuccessful until recently, when perbromate ions were shown to exist by a radioactive tracer technique and the first weighable amount of rubidium perbromate was

obtained by oxidation of bromate ions with xenon difluoride.<sup>2</sup> Subsequent development of the method of oxidizing bromates with elemental fluorine made the large-scale preparation of potassium perbromate feasible.<sup>3</sup> This method was used for the production of the sample used in the present measurements.

The study of the thermodynamic properties of perbromates is of obvious interest, as it furnishes quantitative data relating to the differences between the chemical behavior of heptavalent bromine and that of heptavalent chlorine and iodine. An essential contribution

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. H. Appelman, *J. Amer. Chem. Soc.*, **90**, 1900 (1968).

(3) E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).

in this respect has been made by Johnson, Smith, Appelman, and Hubbard,<sup>4</sup> who determined the enthalpies of formation and solution of potassium perbromate. In the absence of an experimentally established value for the entropy of the compound, however, only an estimate could be given for the Gibbs energy of formation, the most significant thermodynamic datum relevant to the discussion of compound stability. In order to eliminate the uncertainty inherent in the entropy estimate and to gain further information on the thermodynamic characteristics of potassium perbromate, the heat capacity of a 53-g sample was measured from 5 to 350°K. The results of these measurements are reported in this article, together with the thermodynamic functions for the standard state calculated from them.

### Experimental Section

**Potassium Perbromate.**—The calorimetric sample of potassium perbromate was part of the same batch that had been used by Johnson, *et al.*, for heat of decomposition and heat of solution measurements.<sup>4</sup> It was obtained by oxidation of sodium bromate with fluorine gas in alkaline solution as described by Appelman.<sup>3</sup> The oxidizing power of the material was determined by iodometric assay and yielded a value corresponding to 99.94% pure KBrO<sub>4</sub>. Traces of water (0.029 ± 0.003 wt %), of bromate (0.004 mol %), and of fluoride (0.001 mol %) were present, and the concentration of metallic impurities was less than 10 ppm. Before use the salt was stored over Drierite (anhydrous CaSO<sub>4</sub>) in an evacuated desiccator in order to minimize contamination from the atmosphere.

**Calorimetric Apparatus.**—For the thermal measurements 0.29202 mol (53.4415 g) of potassium perbromate was filled into a gold-plated copper calorimeter of 37.1-cm<sup>3</sup> internal volume. The calorimeter itself had previously been used for measurements on ThO<sub>2</sub> and is described in detail by Osborne and Westrum.<sup>5</sup> The lid of the calorimeter was soldered on with 50:50 indium-tin soldering alloy (Cerroseal 35), leaving a pinhole opening on top of a small Monel tube. The pinhole was finally soldered shut after the calorimeter had been placed inside a glass container filled with helium gas at 62 mm pressure. The amount of exchange gas was  $6.54 \times 10^{-6}$  mol.

The heat capacity measurements were carried out with an adiabatic cryostat that has been described in articles by Westrum, Hatcher, and Osborne<sup>6</sup> and by Osborne and Westrum.<sup>5</sup> Although the cryostat has remained essentially unchanged since it was first constructed, a number of changes in the ancillary equipment have recently been made, and the most significant of these will be mentioned briefly.

The temperatures of the top, middle, and bottom of the adiabatic shield and the "floating ring"<sup>5</sup> for the electrical leads are now controlled automatically by means of a four-channel automatic control similar to the one described by Westrum, Furukawa, and McCullough.<sup>7</sup>

Temperatures are measured with a four-lead platinum-encapsulated platinum resistance thermometer (Laboratory designation A-1), which has an ice point resistance of about 25.5 ohms and which is part of the heater-thermometer assembly located inside the reentrant well in the calorimeter. The resistance of the thermometer is determined by comparing the

potential drop across it with the potential drop across a standard resistor by means of a Honeywell Type 2773-S six-dial thermofree double potentiometer and an Electro Scientific Industries Model 900/RO photoelectric galvanometer. The time and the settings of the potentiometer dials are recorded by depressing a key when the galvanometer deflection becomes zero. The sensitivity is  $2.5 \times 10^{-6}$  ohm below 56°K. Above 56°K is  $5 \times 10^{-8}$  ohm, corresponding to  $5 \times 10^{-6}$ °K.

During the heating period the potential drop across the heater (plus one of the two identical current leads between the adiabatic shield and the calorimeter) and the potential drop across a standard resistor are automatically read and recorded several times by means of a Vidar Model 521AR digital voltmeter. The maximum error in any reading is 0.02%. The heater is switched on and the time recorded by depressing a key, and after a preset interval it is automatically switched off by a Wang Model 2019 counter. The time interval has a maximum error of 0.01%.

As in all previous work with this cryostat (except when very long equilibrium times were involved) the temperature drifts before and after each heating period were observed until a steady state was obtained, and the steady-state drifts were used to correct for the slight departure from adiabatic conditions. The temperature scale used for the platinum resistance thermometer (Laboratory designation A-17) has been described previously.<sup>8</sup> All standards of mass, time, resistance, and voltage were traceable to the U. S. National Bureau of Standards.

### Heat Capacities

The data points obtained during the heat capacity measurement of potassium perbromate total 77 in number and are listed in Table I. These points cover the region from 5 to 350°K and include duplicate measurements below 20°K for the purpose of improving the reliability of the results in the low-temperature region. The region between 220 and 290°K was also scanned twice in order to verify the irregularities observed near 245 and 275°K. In each series the temperature increments can be inferred from the difference between the mean temperature of successive points.

Before subtracting the heat capacity of the empty calorimeter, which had been determined in an independent series of measurements and which constituted between 12 and 36% of the measured gross heat capacity, a curvature correction equal to  $-(1/24)(d^2C/dT^2)(\Delta T)^2$  was applied. The curvature correction reduced the gross heat capacity values obtained for temperature increments varying from 2 to 10° to the differential heat capacity value at the mean temperature of the run. In order to obtain the molal heat capacity of potassium perbromate from the curvature-corrected data, the heat capacity of the empty calorimeter was subtracted and an allowance was made for the presence of the small amount of helium exchange gas in the calorimeter and for small changes of the amount of Cerroseal 35 solder and of the Apiezon T grease used to provide thermal contact with the heater. Finally, the molal heat capacities listed in Table I were obtained by division by the number of moles in the sample. The estimated probable error of the data is 0.1% at temperatures above 25°K. Below that temperature the error increases gradually and reaches 5% at 5°K.

The data points of Table I were subjected to a curve-

(4) G. K. Johnson, P. N. Smith, E. H. Appelman, and W. N. Hubbard, *ibid.*, **9**, 119 (1970).

(5) D. W. Osborne and E. F. Westrum, Jr., *J. Chem. Phys.*, **21**, 1884 (1953).

(6) E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, *ibid.*, **21**, 419 (1953).

(7) E. F. Westrum, Jr., G. T. Furukawa, and J. P. McCullough in "Experimental Thermodynamics," Vol. I, J. P. McCullough and D. W. Scott, Ed., Plenum Press, New York, N. Y., 1968, p 168 ff.

(8) D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, *J. Chem. Phys.*, **44**, 2802 (1966).

TABLE I  
 THE HEAT CAPACITY OF KBrO<sub>4</sub><sup>a</sup>

T, °K	C <sub>p</sub> , J deg <sup>-1</sup> mol <sup>-1</sup>	T, °K	C <sub>p</sub> , J deg <sup>-1</sup> mol <sup>-1</sup>	T, °K	C <sub>p</sub> , J deg <sup>-1</sup> mol <sup>-1</sup>
Series 1					
86.088	64.82				
94.555	68.40				
104.935	72.34				
115.907	76.36				
125.965	79.88				
136.122	83.21				
146.153	86.31				
156.073	89.22				
166.099	91.96				
176.051	94.61				
186.011	97.10				
196.003	99.49				
205.966	101.75				
215.794	103.98				
225.794	106.16				
235.803	108.22				
245.776	110.59				
255.752	112.21				
265.798	114.29				
275.855	117.67 <sup>b</sup>				
285.915	117.92				
295.482	119.70				
305.462	121.49				
315.434	123.22				
325.404	124.89				
335.379	126.52				
342.826	127.69				
347.624	128.30				
Series 2					
		265.264	114.14	16.734	6.797
		275.293	117.49 <sup>b</sup>	18.770	9.061
		285.324	117.85	20.690	11.326
Series 3					
		5.702	0.214	22.762	13.863
		7.378	0.502	24.974	16.664
		9.465	1.178	27.462	19.871
		11.607	2.290	30.217	23.889
		13.494	3.684	33.226	27.067
Series 4					
		5.848	0.226	33.875	27.839
		7.903	0.644	37.382	31.829
		9.924	1.368	41.203	35.85
		11.858	2.461	45.193	39.69
		13.837	3.968	49.734	43.64
		15.837	5.865	54.536	47.40
		17.869	8.031		
Series 5					
		17.989	8.179	54.162	47.09
		20.013	10.517	59.333	50.71
		22.075	13.010	65.255	54.38
		24.236	15.725	71.983	58.11
		26.612	18.776	79.196	61.70
		29.262	22.185	87.079	65.29
Series 6					
				95.813	68.89
Series 7					
Series 8					
				226.285	106.29
				236.194	108.37
				246.166	110.63
				256.175	112.26
Series 9					

<sup>a</sup> Molecular weight 183.009; ice point 273.15°K. Corrections for curvature were applied to the data. <sup>b</sup> The heat capacity at this temperature appears to be elevated by approximately 1.3%, probably because of the presence of a small amount (0.3 mol %) of water in the sample. The run was not used in the curve-fitting procedure.

fitting procedure by weighted least squares. The calculation was carried out in double precision on a CDC 3600 computer, and two polynomials in ascending powers of *T* were obtained to represent the data within experimental error in the temperature regions between 5 and 23°K (polynomial degree 7) and between 23 and 350°K (polynomial degree 14).

The heat capacity curve of potassium perbromate is of the simple s-shaped type. There are no obvious irregularities pointing to transitions in the solid state or to other thermal effects attributable to the perbromate. However, four of the heat capacity values of Table I are noticeably elevated above the smooth curve. The entries at *T* = 245.776 and 246.166°K are high by approximately 0.2%, and those at *T* = 275.855 and 275.293°K lie 1.3% above the curve. The reality of the deviations was verified by obtaining two independent measurements in each case which are in very good agreement with each other.

It is easy to find an explanation for the deviation observed near 275°K. Both heat capacity runs involved a 10.0° temperature change from well below the ice point temperature to a temperature above it. Since the freezing point depression of a saturated solution of potassium perbromate (approximately 0.1 *M* at 0°) is expected to be less than 0.5°K, any ice in the sample

should have melted during each of these runs, and the heat required to melt the ice would have caused an apparently high heat capacity. The amount of water calculated from the deviation of the heat capacity at 275°K from the smooth curve is 0.024 wt % H<sub>2</sub>O, in good agreement with the analytical data (*vide supra*). In order to avoid distortion of the heat capacity curve of potassium perbromate the two high heat capacity points at 275°K were not used in the curve-fitting procedure.

The origin of the second irregularity at or near 245°K is not obvious. In fact, the elevation is so slight—of the order of 0.2–0.3%—that it was considered significant only after a second series of data points had been obtained which was found to be in excellent agreement with the data of series 1. The cause of the deviation became apparent during a separate measurement of the heat capacity of a 100-g sample of Cerroseal 35, the 50% indium–50% tin soldering alloy used to attach the cover and close up the calorimeter. Near 245°K the heat capacity curve of Cerroseal 35 shows a small hump, probably because of a solid diffusion process. No correction was made for this hump. The uncertainty in the correction for the Cerroseal 35 causes an uncertainty of less than 0.05% in the heat capacity results for potassium perbromate at all other temperatures.

## Other Thermodynamic Properties

The heat capacities in Table I were, in fact, measured while the sample was exposed to a small pressure of helium which changed with temperature. The correction to a constant pressure of 1 atm, however, is so small that the tabulated data are equal to the standard heat capacities within the experimental uncertainty. Consequently, the polynomial expressions representing these heat capacities could be used for the integration of  $C_P^\circ$  and  $C_P^\circ/T$  in order to calculate the thermodynamic functions in the standard state. The resulting values for the standard entropy,  $S^\circ$ , the enthalpy increment,  $H^\circ - H^\circ_0$ , and the Gibbs energy function,  $-(G^\circ - H^\circ_0)/T$ , at selected temperatures are listed in Table II. Below 6°K the heat capacity was assumed

TABLE II  
THERMODYNAMIC FUNCTIONS OF CRYSTALLINE  
KBrO<sub>4</sub> IN THE STANDARD STATE

T, °K	$C_P^\circ$ , J deg <sup>-1</sup> mol <sup>-1</sup>	$S^\circ$ , J deg <sup>-1</sup> mol <sup>-1</sup>	$H^\circ - H^\circ_0$ , J mol <sup>-1</sup>	$-(G^\circ - H^\circ_0)/T$ , J deg <sup>-1</sup> mol <sup>-1</sup>
6	0.25	0.084	0.38	0.021
10	1.41	0.427	3.26	0.101
15	5.03	1.600	18.33	0.378
20	10.51	3.769	56.68	0.935
25	16.71	6.771	124.52	1.790
30	23.10	10.384	224.10	2.914
35	29.15	14.406	354.93	4.265
40	34.64	18.663	514.66	5.797
45	39.53	23.032	700.34	7.469
50	43.86	27.426	909.04	9.245
60	51.14	36.090	1,385.4	13.000
70	57.07	44.432	1,927.3	16.899
80	62.09	52.389	2,523.7	20.842
90	66.51	59.982	3,167.1	24.772
100	70.52	67.180	3,852.5	28.654
110	74.26	74.078	4,576.6	32.472
120	77.80	80.692	5,337.0	36.217
130	81.19	87.054	6,132.1	39.884
140	84.42	93.190	6,960.3	43.474
150	87.47	99.120	7,819.9	46.987
160	90.35	104.86	8,709.2	50.426
170	93.04	110.42	9,626.2	53.792
180	95.59	115.81	10,570	57.088
190	98.02	121.04	11,538	60.317
200	100.38	126.13	12,530	63.481
210	102.68	131.08	13,545	66.583
220	104.93	135.91	14,583	69.625
230	107.10	140.62	15,643	72.610
240	109.20	145.23	16,725	75.540
250	111.21	149.73	17,827	78.418
260	113.14	154.13	18,949	81.245
270	115.02	158.43	20,090	84.025
273.15	115.60	159.77	20,453	84.890
280	116.87	162.65	21,249	86.758
290	118.70	166.78	22,427	89.446
298.15	120.17	170.09	23,400	91.605
300	120.50	170.83	23,623	92.092
310	122.27	174.82	24,837	94.696
320	123.99	178.72	26,068	97.261
330	125.66	182.57	27,317	99.788
340	127.24	186.34	28,581	102.28
350	128.61	190.05	29,861	104.73

to vary as  $T^3$ . The estimated probable error of the tabulated data is 0.1% except for the region below 20°K,

where it is larger in conformance with the larger errors in the heat capacity. In order to preserve internal consistency, however, the functional values are given to a greater number of places than the estimated probable error would justify.

A comparison of the standard entropy of KBrO<sub>4</sub> at 298.15°K with the estimate published by Johnson, *et al.*,<sup>4</sup> shows the estimated value to be deficient by 12.77 J deg<sup>-1</sup> mol<sup>-1</sup> (7.5%). The recalculation of the standard entropy of formation at 298.15°K from the experimental value  $S^\circ(\text{KBrO}_4, \text{c}) = 170.09 \pm 0.2$  J deg<sup>-1</sup> mol<sup>-1</sup> has the result  $\Delta S_f^\circ(\text{KBrO}_4, \text{c}) = -380.7 \pm 0.8$  J deg<sup>-1</sup> mol<sup>-1</sup>. In this calculation the following values<sup>9</sup> were used for the entropies of potassium, bromine, and oxygen:  $S^\circ(\text{K}, \text{c}) = 64.67 \pm 0.4$  J deg<sup>-1</sup> mol<sup>-1</sup>,  $S^\circ(\text{Br}_2, \text{l}) = 152.2 \pm 1.3$  J deg<sup>-1</sup> mol<sup>-1</sup>, and  $S^\circ(\text{O}_2, \text{g}) = 205.03 \pm 0.04$  J deg<sup>-1</sup> mol<sup>-1</sup>. By inserting  $\Delta S_f^\circ(\text{KBrO}_4, \text{c})$  and  $\Delta H_f^\circ(\text{KBrO}_4, \text{c}) = -287.61 \pm 0.59$  kJ mol<sup>-1</sup> into the equation  $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$ , the standard Gibbs energy of formation of potassium perbromate at 298.15°K is found to be  $\Delta G_f^\circ(\text{KBrO}_4, \text{c}) = -174.10 \pm 0.64$  kJ mol<sup>-1</sup>.

The replacement of the estimated entropy of potassium perbromate by the experimental value also entails changes in the values published by Johnson, *et al.*,<sup>4</sup> for the standard entropy and standard Gibbs energy of formation of perbromate ion and for the standard electrode potential of the bromate-perbromate couple. The revised values at 298.15°K are  $S^\circ(\text{BrO}_4^-, \text{aq}) = 199.8 \pm 1.6$  J deg<sup>-1</sup> mol<sup>-1</sup> and  $\Delta G_f^\circ(\text{BrO}_4^-, \text{aq}) = 118.3 \pm 0.8$  kJ mol<sup>-1</sup>. The revised standard potential of the reaction  $\text{BrO}_3^- + \text{H}_2\text{O} = \text{BrO}_4^- + 2\text{H}^+ + 2\text{e}^-$  is  $1.743 \pm 0.006$  V. The values for the ions are on the conventional scale with  $\Delta H_f^\circ$ ,  $S^\circ$ , and  $\Delta G_f^\circ$  for the hydrogen ion assigned the value zero.

## Discussion

From a comparison of the Gibbs energy of formation of potassium perbromate with the respective values for potassium perchlorate ( $\Delta G_f^\circ(\text{KClO}_4) = -302.1$  kJ mol<sup>-1</sup>) and potassium periodate ( $\Delta G_f^\circ(\text{KIO}_4) = -349.3$  kJ mol<sup>-1</sup>) as given by Johnson, *et al.*,<sup>4</sup> it is at once apparent that the perbromate has a substantially higher Gibbs energy of formation. It is also clear that the entropies of formation do not account for this difference in the Gibbs energies. The formation entropies of potassium perchlorate and potassium periodate<sup>4</sup> are  $\Delta S_f^\circ(\text{KClO}_4) = -435.1$  J deg<sup>-1</sup> mol<sup>-1</sup> and  $\Delta S_f^\circ(\text{KIO}_4) = -373.2$  J deg<sup>-1</sup> mol<sup>-1</sup> (estimated), respectively. These numbers bracket, in fact, the entropy of formation of the perbromate,  $\Delta S_f^\circ(\text{KBrO}_4) = -380.7$  J deg<sup>-1</sup> mol<sup>-1</sup>. The relatively high Gibbs energy of formation of the perbromate is directly attributable to the enthalpy of formation, which has a value of  $-287.6$  kJ mol<sup>-1</sup> and is therewith appreciably more positive than the enthalpy of formation of either the perchlorate ( $\Delta H_f^\circ(\text{KClO}_4) = -431.9$  kJ mol<sup>-1</sup>) or the periodate ( $\Delta H_f^\circ(\text{KIO}_4) = -460.6$  kJ mol<sup>-1</sup>). This higher en-

(9) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., Dec 31, 1969.

thalpy cannot be attributed entirely to a difference in the electrostatic part of the lattice energies. Hence it must reflect the fact that the Br-O bond in  $\text{BrO}_4^-$  is substantially weaker than the halogen-oxygen bonds in the other perhalates.

The Gibbs energy of formation of potassium perbromate, although high by comparison to the other perhalates, is still substantially negative, and by itself it cannot account for the difficulties met in the perbromate synthesis. However, a combination of thermodynamic knowledge with considerations of relative reaction rates leads to a qualitative understanding of the problem. The argument is similar to the one presented by Johnson, *et al.*<sup>4</sup> First of all, we note that the starting material for the synthesis of a perhalate is in general a halate, and halates are the first products of the reduction or decomposition of perhalates. The rate at which the reduction of the perhalates proceeds decreases from periodate, for which the reaction is often extremely fast, over perbromate to perchlorate, for which it is usually extremely slow. This suggests that the energy of activation for the reduction of the perhalates is highest for perchlorate and has successively lower values for perbromate and periodate:  $E_a(\text{KClO}_4) > E_a(\text{KBrO}_4) > E_a(\text{KIO}_4)$ . The respective energies of activation for the reverse reactions, the oxidation of the halates along the same reaction paths, include the Gibbs energy difference between perhalate and halate in addition to the energy of activation of the forward reaction. For the three pairs of potassium salts,  $\text{KClO}_4$ - $\text{KClO}_3$ ,  $\text{KBrO}_4$ - $\text{KBrO}_3$ , and  $\text{KIO}_4$ - $\text{KIO}_3$ , the Gibbs energy differences are -5.9, 96.5, and 67.4 kJ mol<sup>-1</sup>, respectively. It is now easy to see that it will be the energy of activation for the bromate oxidation which experiences the largest increase, nearly 100 kJ mol<sup>-1</sup>. This may well boost its already fairly high value to a height at which the bromate oxidation becomes extremely slow and difficult to achieve, as is borne out by experimental observations.

It is interesting to compare the ionic standard entropies of the halates and perhalates with values calculated from expressions which correlate entropies with ionic properties such as mass, size, and structure. A number of such correlation functions have been proposed. However, we shall restrict our attention to those of Cobble,<sup>10</sup> of Connick and Powell,<sup>11</sup> and of Couture and Laidler,<sup>12</sup> because they are specifically applicable to anions of oxy acids. The pertinent data have been assembled in Table III. No experimental number is available for the entropy of the periodate ion, which has been estimated as 204 J deg<sup>-1</sup> mol<sup>-1</sup> by Johnson, *et al.*<sup>4</sup>

Inspection of Table III shows that the agreement between the experimental and calculated values in general is not very good. We must take into consideration, however, that the correlation functions were de-

TABLE III  
STANDARD IONIC ENTROPIES ( $J \text{ DEG}^{-1} \text{ MOL}^{-1}$ ) FOR THE  
HALATE AND PERHALATE IONS IN AQUEOUS SOLUTION;  
 $S^\circ(\text{H}^+, \text{aq}) \equiv 0$

Ion	Exptl value	Calcd values		
		a	b	c
$\text{ClO}_3^-$	$162.3 \pm 1.5$	161.7	150.9	193.7
$\text{BrO}_3^-$	$161.5 \pm 1.5$	187.2	150.9	202.4
$\text{IO}_3^-$	$118.4 \pm 1.5$	202.6	150.9	208.5
$\text{ClO}_4^-$	$182.4 \pm 1.7$	160.4	205.4	208.7
$\text{BrO}_4^-$	$199.8 \pm 1.6$	182.2	205.4	215.4
$\text{IO}_4^-$	...	201.4	205.4	221.0

<sup>a</sup> Entropies in this column were calculated from eq 2 given by Cobble.<sup>10</sup> <sup>b</sup> Entropies in this column were calculated from eq 1 given by Connick and Powell.<sup>11</sup> <sup>c</sup> Entropies in this column were calculated from eq 2 given by Couture and Laidler.<sup>12</sup>

rived from entropy data for many different classes of ions, even though all of them were anions of oxy acids. In representing the entropy variation among the different classes the correlation functions generally are useful. If applied to a single group of very similar ions, such as the group of the three halate ions or the group of the three perhalate ions, they fail to account for the entropy differences among the individual members. This is obvious in the case of the equation of Connick and Powell, since it assigns equal entropies to ions of like structure and charge. That this equation nevertheless approximates the entropies for a wide variety of ionic species only demonstrates the preponderant influence of the number of charge-bearing oxygen atoms upon the entropy of an oxy acid anion.

An entry in Table III which deserves some attention is the low value for the entropy of the iodate ion,  $\text{IO}_3^-$ . It fails to conform to any of the correlation functions. Scrutiny of the experimental data reveals the principal reason for the deficiency, namely, the comparatively small enthalpy of solution of  $\text{KIO}_3$ . While the enthalpies of solution of potassium chlorate and bromate are 41.38 and 40.79 kJ mol<sup>-1</sup>, respectively, that of potassium iodate is only 27.74 kJ mol<sup>-1</sup>.<sup>13</sup> An explanation for the exceptional behavior of the iodate ion has yet to be found. Possibly it might be the result of the formation of a hydrated species, such as  $\text{H}_2\text{IO}_4^-$ , although experimental evidence is lacking, or it might be argued that a special interaction of the iodate ion with the native structure of the water is involved. In that case the low entropy value would indicate a strongly reinforcing influence upon the hydrogen-bonded molecular aggregates presumed to be present in the water, an influence which would have to originate from the particular structural and dimensional properties of the iodate ion.

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