perimentally obtained diffusion currents and thus offer an explanation for the anomalous diffusion current constant in the case of samarium.

Acknowledgment.—This work was undertaken while one of us (A. T.) held a graduate college research assistantship at the State University of Iowa.

Summary

Solutions of samarium chloride and sulfate were studied polarographically without supporting electrolyte and in the presence of lithium chloride, potassium chloride and tetramethylammonium iodide. Addition of sulfuric acid to the sulfate solutions stabilized the half-wave potential. With one millimolar samarium ion, in 0.001 normal sulfuric acid, 0.1 molar tetramethylammonium iodide and 0.01% gelatin medium a two step polarogram was obtained. The half-wave potentials were −1.80 and −1.96 volts against the saturated calomel electrode. The diffusion currents were, respectively, 6.0 and 13.0 microamp., corresponding to $Sm^{+++} \rightarrow Sm^{++}$, and $Sm^{++} \rightarrow Sm^0$. However, in 4 millimolar solution the behavior is anomalous.

IOWA CITY, IOWA RECEIVED JUNE 9, 1947

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies of $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$, and $CaO \cdot 2B_2O_3$[1]

BY K. K. KELLEY,[2] S. S. TODD[3] AND C. H. SHOMATE[4]

In a recent paper, Torgeson and Shomate[5] presented data for the heats of formation of the crystalline calcium borates, $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$, and $CaO \cdot 2B_2O_3$. These are all the compounds in the $CaO–B_2O_3$ system, according to the work of Carlson.[6] The present paper reports low temperature heat capacity and entropy determinations of these same substances, thus enabling the calculation of their free energies of formation. There are no previous similar data for any of these compounds.

Materials.—The samples of calcium borates used in the present measurements were virtually the same as those employed in the heat of formation studies of Torgeson and Shomate.[5] Their paper included the method of preparation of the samples, their densities, and X-ray diffractions, and repetition here appears unnecessary. About one mole of each compound was used in the present measurements and all weighings were corrected to vacuum. The chemical purity of the samples is indicated by the following analyses:

Substance	Actual analysis CaO, %	Actual analysis B_2O_3, %	Theoretical analyses CaO, %	Theoretical analyses B_2O_3, %
$3CaO \cdot B_2O_3$	70.75	29.31	70.72	29.28
$2CaO \cdot B_2O_3$	61.71	38.41	61.69	38.31
$CaO \cdot B_2O_3$	44.59	55.26	44.61	55.39
$CaO \cdot 2B_2O_3$	28.57	71.02	28.71	71.29

Only the calcium diborate contained any appreciable impurity. As mentioned by Torgeson and Shomate,[5] this material contained 0.42% of insoluble impurity from superficial reaction with the nickel crucible in which it was prepared. No correction for this impurity was made in the present results.

Heat Capacities.—The heat capacities were measured by means of previously described[7] apparatus and methods. The results, expressed in defined calories,[8] are listed in Table I and shown graphically in Fig. 1. The molecular mass figures in the headings of Table I accord with the 1947 International Atomic Weights.[9] The precision error in the results is under 0.1% and it is believed they are accurate on the average to within ±0.3% in the absolute sense.

The heat capacities of all four calcium borates are higher at the lower temperatures, and lower at the higher temperatures, than the sum of the heat capacities of the component oxides. The greatest average deviation from additivity is shown by $CaO \cdot 2B_2O_3$, the heat capacity of which averages over 2 cal. per deg. per mole lower than the sum of the heat capacities of the component oxides in the temperature range 100 to 298.16°K. In this connection it is of interest to note that this substance also has the highest atomic density (lowest mean atomic volume). Other things being equal, high atomic density generally parallels low heat capacity at low temperatures.

Entropies at 298.16°K.—In each instance, the entropy increment between 52.00 and 298.16°K. (measured portion, Table II) was obtained, as usual, by numerical integration of a large-scale plot of C_p against log T. To obtain the entropy

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[5] Torgeson and Shomate, THIS JOURNAL, **69**, 2103 (1947).

[6] Carlson, *Bur. Standards J. Research*, **9**, 825 (1932).

[7] Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper* 686 (1946).

[8] Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

[9] Baxter, Guichard and Whytlaw-Gray, THIS JOURNAL, **69**, 731 (1947).

TABLE I

MOLAL HEAT CAPACITIES

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
	$3CaO·B_2O_3$ (mol. wt., 237.88)		
52.8	5.978	165.5	30.66
56.6	6.827	175.5	32.13
60.6	7.806	185.6	33.52
64.9	8.863	195.9	34.82
69.0	9.932	205.9	36.09
73.5	11.13	216.2	37.23
77.7	12.21	226.2	38.28
84.7	14.02	235.8	39.27
94.8	16.56	246.1	40.35
104.6	18.92	256.1	41.29
115.1	21.34	266.1	42.22
125.1	23.47	276.2	43.18
135.1	25.45	286.1	43.82
145.7	27.39	296.3	44.77
155.5	29.07	(298.16)	(44.90)
	$2CaO·B_2O_3$ (mol. wt., 181.80)		
53.0	4.914	165.7	23.91
57.0	5.695	175.6	25.04
61.1	6.522	185.8	26.10
65.5	7.399	195.9	27.10
69.8	8.295	206.2	28.08
74.1	9.191	216.2	29.00
78.4	10.06	226.0	29.84
85.6	11.49	235.8	30.60
94.8	13.27	246.2	31.43
104.5	15.03	256.2	32.30
115.2	16.87	266.5	33.07
125.2	18.46	276.2	33.71
135.1	19.96	286.1	34.39
145.4	21.37	296.5	35.03
155.5	22.67	(298.16)	(35.16)
	$CaO·B_2O_3$ (mol. wt., 125.72)		
54.4	4.199	145.5	14.93
56.9	4.554	155.6	15.81
57.7	4.679	165.8	16.68
60.4	5.064	179.1	17.70
61.8	5.265	185.6	18.15
64.4	5.634	195.8	18.87
68.5	6.220	205.4	19.58
71.2	6.604	216.0	20.21
72.6	6.795	226.1	20.84
75.6	7.233	235.4	21.40
80.8	7.924	245.2	21.98
84.8	8.455	255.6	22.55
94.0	9.580	265.5	23.16
104.2	10.80	276.1	23.73
114.3	11.93	286.4	24.24
124.3	12.96	296.3	24.78
135.3	14.02	(298.16)	(24.85)
	$CaO·2B_2O_3$ (mol. wt., 195.36)		
54.2	4.583	165.7	21.75
57.5	5.092	175.9	23.11
61.6	5.742	189.0	24.84
66.6	6.558	196.0	25.76
71.5	7.366	206.3	27.07
76.3	8.148	215.9	28.31
81.4	8.998	226.4	29.61
86.3	9.776	235.8	30.74
94.4	11.07	245.6	31.88
104.5	12.65	256.0	33.20
114.6	14.22	266.0	34.30
124.1	15.67	276.2	35.33
135.9	17.42	286.5	36.42
146.0	18.90	296.5	37.56
155.8	20.31	(298.16)	(37.75)

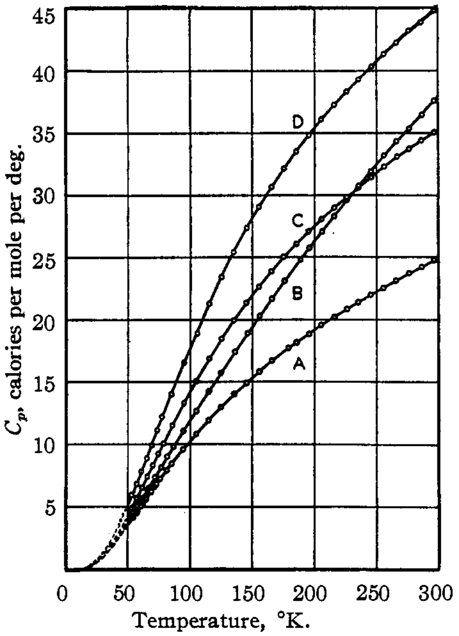

Fig. 1.—Heat capacities: A, $CaO·B_2O_3$; B, $CaO·2B_2O_3$; C, $2CaO·B_2O_3$; D, $3CaO·B_2O_3$.

increments between 0 and 52.00°K., the measured heat capacities were fitted with the following combinations of Debye and Einstein functions, the maximum deviation between measurements and function sums being shown in parentheses

$$3CaO·B_2O_3 \quad 4D\left(\frac{332}{T}\right) + 4E\left(\frac{534}{T}\right) + 3E\left(\frac{1362}{T}\right) \quad (0.5\%)$$

$$2CaO·B_2O_3 \quad 3D\left(\frac{316}{T}\right) + 3E\left(\frac{511}{T}\right) + 3E\left(\frac{1330}{T}\right) \quad (0.5\%)$$

$$CaO·B_2O_3 \quad 2D\left(\frac{280}{T}\right) + 2E\left(\frac{503}{T}\right) + 3E\left(\frac{1328}{T}\right) \quad (1.0\%)$$

$$CaO·2B_2O_3 \quad 3D\left(\frac{334}{T}\right) + 4E\left(\frac{700}{T}\right) + 3E\left(\frac{1217}{T}\right) \quad (1.0\%)$$

These function sums were employed in obtaining the extrapolated portions of the entropies in Table II. The extrapolated portion constitutes

TABLE II

ENTROPIES AT 298.16°K., CAL./DEG./MOLE

	$3CaO·B_2O_3$	$2CaO·B_2O_3$	$CaO·B_2O_3$	$CaO·2B_2O_3$
0°–52.00°K., (extrapolation)	2.16	1.84	1.65	1.59
52.00°–298.16°K., (measured)	41.73	32.84	23.41	30.61
$S^0_{298.16}$	43.9 ± 0.3	34.7 ± 0.2	25.1 ± 0.2	32.2 ± 0.3

only 6.6% of the total entropy for $CaO \cdot B_2O_3$ and is lower for the other substances.

The entropies of $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, and $CaO \cdot B_2O_3$ differ, in order, by 9.2 and 9.6 units, corresponding to successive decreases of one mole of calcium oxide. These figures are to be compared with the measured value for free calcium oxide,[10] $S^0_{298.16} = 9.5 \pm 0.2$. This type of approximate additivity of entropies of some inter-oxidic compounds has been noted previously in work of this Laboratory and is the result of compensation of plus and minus deviations from additivity of heat capacities. In the case of $CaO \cdot 2B_2O_3$ such compensation is quite incomplete and the entropy difference between $CaO \cdot 2B_2O_3$ and $CaO \cdot B_2O_3$ is only 7.1 units, whereas the entropy of crystalline boric oxide[11] is $S^0_{298.16} = 13.0 \pm 0.1$.

Related Thermal Data.—Free energies of formation at 298.16°K. of the four calcium borates from the oxides and from the elements are given in Table III, being obtained from the relationship $\Delta F^0 = \Delta H - T\Delta S$. The heats of formation, $\Delta H_{298.16}$, are from the paper of Torgeson and Shomate.[5] The entropies employed in calculation of the $\Delta S_{298.16}$ values are from publications of Kelley.[10,11]

Precision uncertainties have been assigned to the free energies of formation from the oxides. It is not possible to do this for the values from the elements because the probable error in the heat of formation of crystalline boric oxide, on which the free energies depend, is not known.

TABLE III

FREE ENERGIES OF FORMATION AT 298.16°K., CAL./MOLE

Substance	$\Delta H_{298.16}$	$\Delta S_{298.16}$	$\Delta F^0_{298.16}$
	From oxides		
$3CaO \cdot B_2O_3$	$-60,000 \pm 40$	2.4 ± 0.7	$-60,720 \pm 210$
$2CaO \cdot B_2O_3$	$-45,760 \pm 30$	2.7 ± 0.5	$-46,570 \pm 150$
$CaO \cdot B_2O_3$	$-29,420 \pm 20$	2.6 ± 0.3	$-30,200 \pm 90$
$CaO \cdot 2B_2O_3$	$-42,930 \pm 20$	-3.3 ± 0.5	$-41,950 \pm 150$
	From elements		
$3CaO \cdot B_2O_3$	$-858,200$	-136.4 ± 0.6	$-817,500$
$2CaO \cdot B_2O_3$	$-692,100$	-111.2 ± 0.5	$-659,000$
$CaO \cdot B_2O_3$	$-524,000$	-86.3 ± 0.5	$-498,300$
$CaO \cdot 2B_2O_3$	$-880,200$	-156.2 ± 0.9	$-833,700$

The free energy of formation values from the oxides follow a normal pattern. The formation of $CaO \cdot B_2O_3$ from the oxides gives a decrease in free energy of 30,200 cal. Smaller decreases in free energy accompany each successive step of adding one mole of oxide to $CaO \cdot B_2O_3$ to form the other calcium borates.

Summary

Low temperature heat capacity measurements of $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$, and $CaO \cdot 2B_2O_3$ were made throughout the temperature range 52° to 298.16°K.

The entropies of the four calcium borates were determined as 43.9 ± 0.3, 34.7 ± 0.2, 25.1 ± 0.2, and 32.2 ± 0.3 cal./deg./mole, respectively.

Free energy of formation values from the oxides and from the elements are included.

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[10] Kelley, *Bur. Mines Bull.*, 434 (1941).

[11] Kelley, THIS JOURNAL, **63**, 1137 (1941).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1154]

The Reactions of Antiserum Homologous to the *p*-Azosuccinanilate Ion Group[1a]

BY DAVID PRESSMAN,[1b] JOHN H. BRYDEN AND LINUS PAULING

It was discovered by Landsteiner and van der Scheer[2] that the precipitation of azoprotein containing the *p*-azosuccinanilate ion haptenic group by hapten-homologous antiserum (anti-S_p serum) is inhibited just as well by maleate ion as by succinate ion, whereas fumarate ion is practically ineffective, and from this observation the cautious conclusion was drawn[3,4] that "Accordingly, one could suppose that the succinic acid molecule can exist in a form corresponding to the *cis* configuration, or that the antibodies adjust themselves to this." Because of our interest in the use of immunochemical techniques for the determination of the configuration of molecules and haptenic groups,[5] we have extended our quantitative studies of hapten inhibition of serological precipitation to include the S_p system, and have investigated the effect of over fifty haptens on the precipitation of S_p-ovalbumin and anti-S_p serum. The analysis of the data has shown that the normal configuration of the *p*-azosuccinanilate ion group in aqueous solution is a *cis* configuration, presumably stabilized by a hydrogen bond, and has provided information about the configuration of other ions.

Experimental Methods

Haptens.—The following substances used in this work have been described previously[6]: succinanilic acid, *p*-aminosuccinanilic acid, *p*-nitrosuccinanilic acid, and *d*-

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[1a] The Serological Properties of Simple Substances. XIII. For No. XII of this series see D. Pressman, A. L. Grossberg, L. H. Pence, and L. Pauling, THIS JOURNAL, **68**, 250 (1946).

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[3] K. Landsteiner, "The Specificity of Serological Reactions," Charles C Thomas, Springfield, Illinois, 1936, p. 129.

[4] K. Landsteiner, "The Specificity of Serological Reactions," Revised Edition, Harvard University Press, Cambridge, Mass., 1945, p. 192.

[5] D. Pressman, *Register of Phi Lambda Upsilon*, **29**, 30 (1944).

[6] D. Pressman, J. H. Bryden, and L. Pauling, THIS JOURNAL, **67**, 1219 (1945).