Report No. CCC-1024-TR-240

THERMODYNAMICS
OF SODIUM TETRAMETHOXYBORATE
AND TETRAMETHOXYBORATE ION

BOSTON UNIVERSITY
Boston, Massachusetts

May 6, 1957

C A L L E R Y • P E N N S Y L V A N I A

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

May 6, 1957

THERMODYNAMICS OF SODIUM TETRAMETHOXYBORATE
AND TETRAMETHOXYBORATE ION

by

L. V. Coulter

J. R. Sinclair

BOSTON UNIVERSITY
Boston, Massachusetts

for

CALLERY CHEMICAL COMPANY
Callery, Pennsylvania

Technical Editor: M. G. Haddaway

Submitted by:

A. D. McElroy
A. D. McElroy,

Supervisor, Research Department

Approved by:

G. F. Huff
G. F. Huff,

Director of Research and Development

ABSTRACT

The heat capacity of sodium tetramethoxyborate has been determined from 14° to 300°K by means of an adiabatic calorimeter. At 298.15°K the entropy was found to be 68.60 cal. deg.⁻¹ mole⁻¹; the heat content ($H^\circ - H_0^\circ$), 1037 cal. mole⁻¹; and the heat capacity, 54.70 cal. deg.⁻¹ mole⁻¹. The heat of solution in liquid ammonia at -33°C was found to be 0.0 kcal. $\pm$ 1 kcal. For the solution reaction of solid sodium tetramethoxyborate in liquid ammonia at -33°, $\Delta F^\circ = 4.1$ kcal. and $\Delta S^\circ = -17 \pm 3$ cal. deg.⁻¹ mole⁻¹. Relative to $S^\circ [H^+(am)] = 0$ in liquid ammonia at -33°C, $\bar{S}^\circ [B(OCH_3)_4^-(am)] = 28 \pm 3$ cal. deg.⁻¹ mole for the tetramethoxyborate ion in the hypothetical one molal solution.

CONTENTS

ABSTRACT	i
INTRODUCTION	1
RESULTS AND DISCUSSION	1
EXPERIMENTAL	7
REFERENCES	9

INTRODUCTION

The quantitative prediction of chemical reactions involving boron compounds has been limited by the paucity of thermodynamic data for these substances. As a consequence, boron compounds have received increased attention as part of a general effort to establish a body of thermodynamic data which will permit interpretations and predictions of reactions involving boron and its compounds.

As part of this general interest, the entropy of sodium tetramethoxyborate has been determined, and will make possible the calculation of its free energy of formation when its heat of formation has been determined. In addition to the determination of the entropy of sodium tetramethoxyborate, its heat of solution in liquid ammonia has been measured at -33°C in order to obtain an estimate of the entropy of the tetramethoxyborate ion in liquid ammonia, since very little, if any, information is available for large ions in this solvent.

RESULTS AND DISCUSSION

The experimental values of the heat capacity of sodium tetramethoxyborate are tabulated as shown in Table I (page 2). The entropy and heat content have been computed, graphically, from plots of C_p/T vs. T and C_p vs. T , respectively. Smooth values of the heat capacity, entropy, and heat content were tabulated and are presented in Table II (page 3 and 4).

From 0° to 14.36°K , the entropy contribution was estimated by means of a Debye extrapolation. From 14° to 35°K , the heat capacity was best represented by the Debye function $C_p = 2.7 D (136/T)$.

The heat of solution of sodium tetramethoxyborate in ammonia could not be determined with accuracy because of its low solubility in liquid ammonia at -33°C . Two heat-of-solution experiments were made using sample weights of 0.2069 and 0.2342 g. In each experiment, a net observable heat effect did not accompany the solution process, which was completed in less than 10 minutes. Assuming that the heat of dilution is small, the solution reaction may be represented by

The Partial Molal Ionic Entropy of $\text{B}(\text{OCH}_3)_4^-$ in Ammonia

For the calculation of the standard free energy of solution of sodium tetramethoxyborate to give the hypothetical 1 M solution, the following equilibrium reaction may be written:

TABLE I

Experimental Heat Capacity Data for Sodium Tetramethoxyborate

<u>T</u> <u>(°K)</u>	<u>C_p</u> <u>(cal. mole⁻¹ deg. ⁻¹)</u>	<u>T</u> <u>(°K)</u>	<u>C_p</u> <u>(cal. mole⁻¹ deg. ⁻¹)</u>
14.358	1.373	132.280	35.62
16.313	2.076	138.832	36.63
19.090	3.003	145.199	37.59
22.147	4.122		
26.046	5.394	143.650	37.38
29.916	6.749	149.683	38.23
32.992	7.831	155.837	39.00
35.625	8.825	162.088	39.96
37.950	9.689	168.441	40.75
40.371	10.63	175.025	41.53
43.086	11.68	181.831	42.34
46.255	12.91	188.506	43.09
49.628	14.19	195.064	43.79
52.686	15.33	201.800	44.50
55.726	16.41		
58.982	17.50	201.564	44.48
62.409	18.71	208.132	45.16
65.807	19.76	215.095	45.85
		222.168	46.56
66.968	20.18	229.276	47.31
70.538	21.33	236.421	48.04
73.914	22.34	243.460	48.68
77.668	23.50	250.392	49.47
81.612	24.66		
86.128	25.99	249.767	49.37
92.295	27.46	256.520	50.10
99.371	29.13	263.168	50.77
106.039	30.64	269.724	51.48
112.393	31.99	276.658	52.22
118.784	33.20	284.365	53.06
125.510	34.45	292.344	54.01
		300.187	54.93

TABLE II

Molar Entropy, Heat Content, and Heat Capacity of Sodium Tetramethoxyborate

<u>T</u> <u>(°K)</u>	<u>S°</u> <u>(e.u.)</u>	<u>H° - H°</u> <u>(cal. mole⁻¹)</u>	<u>C_p°</u> <u>(cal. mole⁻¹ deg. ⁻¹)</u>
14.358	0.508	15.1	1.37
15	0.576	16.1	1.59
20	1.273	28.3	3.30
25	2.196	49.0	4.99
30	3.270	78.4	6.75
35	4.450	116.7	8.60
40	5.719	164.5	10.49
45	7.065	221.7	12.41
50	8.473	288.4	14.30
55	9.925	364.6	16.15
60	11.41	449.6	17.87
65	12.90	543.1	19.54
70	14.41	645.0	21.16
75	15.92	754.6	22.69
80	17.44	872.0	24.19
85	18.95	996.3	25.61
90	20.45	1128.	26.90
95	21.93	1265.	28.12
100	23.41	1409.	29.29
105	24.86	1558.	30.42
110	26.30	1713.	31.50
115	27.72	1873.	32.50
120	29.13	2037.	33.44
125	30.51	2207.	34.33
130	31.88	2381.	35.24
135	33.22	2559.	36.04
140	34.55	2741.	36.82
145	35.85	2929.	37.56
150	37.14	3117.	38.28
155	38.40	3311.	39.00

TABLE II (cont.)

<u>T</u> <u>(° K)</u>	<u>S°</u> <u>(e.u.)</u>	<u>H° - H°</u> <u>(cal. mole⁻¹)</u>	<u>C_p°</u> <u>(cal. mole⁻¹ deg. ⁻¹)</u>
160	39.65	3507.	39.70
165	40.88	3707.	40.33
170	42.10	3909.	40.94
175	43.29	4116.	41.55
180	44.47	4327.	42.13
185	45.63	4537	42.69
190	46.78	4753	43.27
195	47.91	4969.	43.79
200	49.03	5190.	44.32
205	50.12	5412.	44.84
210	51.21	5639.	45.34
215	52.28	5866.	45.84
220	53.34	6098.	46.34
225	54.39	6331.	46.87
230	55.42	6566.	47.39
235	56.45	6804.	47.89
240	57.46	7045.	48.42
245	58.46	7289.	48.91
250	59.46	7535.	49.44
255	60.44	7781.	49.94
260	61.41	8033.	50.46
265	62.38	8288.	50.99
270	63.34	8543.	51.52
275	64.29	8803.	52.04
280	65.23	9063.	52.57
285	66.17	9329.	53.15
290	67.10	9594.	53.87
295	68.02	9866.	54.37
298.15	68.60	10037.	54.70
300	68.94	10140.	54.89

In this reaction, it is assumed that anammonous sodium tetramethoxyborate is the stable phase in equilibrium with the saturated solution at 240°K. At saturation, the molality³ is 0.13 and the mean activity coefficient was estimated to be 0.1 on the basis of existing data for mono-monovalent electrolytes in liquid ammonia.⁴ Accordingly,

$$\begin{aligned}\Delta F^\circ &= RT \ln K = -RT \ln (\gamma_{\pm} m)^2 \\ &= -RT \ln (0.1 \times 0.13)^2 = 4.1 \text{ kcal.} \pm 0.3 \text{ kcal.}\end{aligned}$$

For the entropy of solution, a value of

$$\begin{aligned}\Delta \bar{S}^\circ &= (\Delta H^\circ - \Delta F^\circ)/T \\ &= (0.0 - 4100)/240 = -17 \pm 3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}\end{aligned}$$

was obtained. For the tetramethoxyborate ion in the hypothetical one molal solution in liquid ammonia (relative to $\bar{S}^\circ [H^+(am)] = 0$), the relative partial molal ionic entropy is

$$\begin{aligned}\bar{S}^\circ_{240^\circ K} &= \Delta \bar{S}^\circ_{\text{solv.}} - \bar{S}^\circ [Na^+] + S^\circ [NaB(OCH_3)_4] \\ &= -17 - 12.6 + 57.5 = 28 \pm 3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.\end{aligned}$$

The entropy of an ion in solution may be regarded as the sum of the gas ion entropy and the entropy change associated with the solvation process when the gas ion is introduced into the solvent, i. e.,

$$\bar{S}^\circ(\text{absolute}) = \bar{S}^\circ(\text{relative}) + \text{constant} = \bar{S}^\circ(\text{gas}) = \Delta \bar{S}^\circ(\text{solvation}).$$

For monovalent monatomic ions, the relative $\Delta \bar{S}^\circ(\text{solvation})$ appears to depend linearly on $1/r^5$ (r = univalent radius) and represents the entropy change associated with the solvent in addition to the loss of translational entropy of the monatomic ion for the reaction $A^-(\text{gas}) = A^-(\text{solution})$. For polyatomic ions, $\Delta \bar{S}^\circ(\text{solvation})$ also may include any net change in rotational or vibrational entropy for the previous reaction. In principle, it is, therefore, possible to compare (-1) polyatomic with (-1) monatomic ions of the same or similar radii, provided $\bar{S}^\circ(\text{relative})$ and $\bar{S}^\circ(\text{gas})$ are known. The former of these properties is measurable, experimentally, but the latter must be calculated and, for the more complicated ions such as $B(OCH_3)_4^-$, this calculation is made difficult by the absence of molecular constant data and vibrational frequency assignments.

In order to make a purely empirical comparison of relative ionic entropies, $\bar{S}^\circ(\text{relative})$ vs. $1/r$ for the negative ions (for which data^{1,6} now exist for ammonia solutions), has been plotted as shown in Figure 1 (page 6). With the exception of I^- , the relative ionic entropy is a linear function of $1/r$ for a group of ions which are considerably different in structure. This is possibly a fortuitous circumstance; however this empirical method may be used to estimate unknown ionic entropies in place of experimental information.

Figure 1
Relative Ionic Entropies

The comparisons should be made through the ΔS° (solvation) for the reaction: Ion (gas) $\longrightarrow$ Ion (solution). In Figure 2, (page 8) $\bar{S}^\circ$ (relative) + constant $-\bar{S}^\circ$ (gas) for I^- , Cl^- , BH_4^- , NH_2^- , and NO_3^- has been plotted. Within experimental error, ΔS solvation for the polyatomic ions NO_3^- , BH_4^- , NH_2^- is in agreement with the ΔS solvation expected for monatomic ions of similar radii. This signifies that these polyatomic ions undergo little, if any, net loss of rotational and vibrational entropy and, hence, retain their rotational and vibrational degrees of freedom characteristic of the gas state. (Any loss of rotational or vibrational entropy would lead to solvation entropies more negative than those observed for monatomic ions; however this is not the situation.)

It is possible that the rotational motion is, in part, replaced by a vibrational motion which has essentially the same entropy contribution to the ionic entropy.

The lack of information regarding the vibrational degrees of freedom of the $B(OCH_3)_4^-$ ion does not permit evaluation of the entropy of vibration of this gas ion. For $\bar{S}^\circ$ (translation + rotation) values of 60 cal. deg⁻¹ mole⁻¹ and the relative $\Delta \bar{S}^\circ$ (solvation) = -32 cal. deg⁻¹ mole⁻¹ (excluding the vibrational entropy from consideration) were estimated. The difference (24 cal. deg⁻¹ mole⁻¹) between this value for ΔS and that to be expected for a monatomic ion is a reasonable value for the vibrational entropy of the tetramethoxyborate ion; but a quantitative comparison is not possible at this time.

EXPERIMENTAL

The sodium tetramethoxyborate, obtained from Callery Chemical Company, was used in all measurements without further purification. The following analysis was furnished by the supplier: anal. calc'd. boron 6.83 percent (6.85 percent theoretical); sodium 14.50 percent (theoretical 14.55 percent).

The heat capacity measurements were made in a low temperature calorimeter described in a previous report.¹ The heat of solution measurements in liquid ammonia were made in a calorimeter described by Coulter and Maybury.² All samples were loaded in a dry box. A sample weighing 57.061 g. in vacuo (0.36125 mole) was employed in the heat capacity measurements.

The heat capacity measurements were made between 14.36°K and 300.19°K in five series of runs, each of which consisted of consecutive measurements. The five overlapping sections of the heat capacity curve joined smoothly; abnormal behavior was not observed.

The absolute temperature of the ice point was taken to be 273.15°K, and one calorie was taken to be 4.1833 international joules.

Figure 2

Relative Entropy of Solvation
of Gas Ions in Liquid Ammonia

REFERENCES

1. L. V. Coulter, J. R. Sinclair, and A. Cole, Final Report, Part 3 to Callery Chemical Company, January 26, 1957, "The Thermodynamics of Sodium Amide."
2. L. V. Coulter and R. H. Maybury, J. Am. Chem. Soc., 71, 3398 (1949)
3. Letter from E. B. Ayres to L. V. Coulter, May 21, 1954
4. J. Sedlet and T. Devries, J. Am. Chem. Soc., 73, 5808 (1951)
5. K. J. Laidler, Canadian J. of Research, 34, 1107 (1956). See also R. E. Powell and W. M. Latimer, J. Chem. Physics, 19, 1139 (1951)
6. L. V. Coulter et. al., Callery Chemical Company, CCC-1024-TR-218, January 7, 1957; L. V. Coulter, J. Phys. Chem., 57, 553 (1953); W. M. Latimer and W. L. Jolly, J. Am. Chem. Soc., 75, 4147 (1953)