in anhydrous salts the $(CH_3)_2Sn^{++}$ ion resembles $:Sn^{++}$ (where the pair of dots indicates the unused $5s^2$ electrons in the latter), and should also resemble: Pb^{++} and $:Tl^+$ in structure.[10,11]

We have compared the properties and solubilities of salts of $(CH_3)_2Sn^{++}$, Pb^{++} and Sn^{++} ions in Table I, and we note especially the formation of basic salts like $PbO{\cdot}PbCrO_4$ which resemble the basic dimethyltin salts described herein. The similarities are striking, and provide support for the view that the $(CH_3)_2Sn^{++}$ ion has the structure indicated above. It is equally certain that $(CH_3)_2Sn^{++}$ does *not* resemble tetravalent tin in the nature and behavior of its compounds.

TABLE I

COMPARISON OF SOLUBILITIES

Salt	Sn^{++}[c,d]	$(CH_3)_2Sn^{++}$	Pb^{++}[d]
Acetate		Sol[a]	$19.7^{0°}$
Antimonate	Insol.	Insol.	Insol.
Arsenate	Insol.	Insol.	Insol.
Azide	Insol.	Insol.	Insol.
Borate	Insol.	Insol. (meta)	Insol. (meta)
Bromate	...	(No ppt.)	$1.38^{20°}$
Bromide	Sol.	Sol.[a]	$0.45^{0°}$
Chlorate	...	(No ppt.)	$151^{18°}$
Chloride	$83.9^{0°}$[f]	$120^{25°}$	$0.673^{0°}$
Chromate (basic)	...	Insol.	Insol.
Chromate	Insol.	...	Insol.
Cyanate	...	Insol.	Insol.
Cyanide	...	Insol.	V. sl. sol.
Ferricyanide	Insol.	V. sl. sol.	Sl. sol.
Ferrocyanide	Insol.	Insol.	Insol.
Fluoride	Sol.[e]	$466^{20°}$[b]	$0.064^{20°}$
Formate	...	Sol.[a]	$1.6^{18°}$
Phosphite	Insol.	Insol. (hypo)	...
Iodate	...	Insol.	$0.0012^{0°}$
Iodide	$1.3^{21°}$	Sol.[a]	0.0442
Molybdate	...	Insol.	Insol.
Nitrate	Sol.	Sol.	$38.8^{0°}$
Nitrite	...	Insol.	...
Oxalate	Insol.	Insol.	1.6×10^{-4} $^{18°}$
Oxide	...	Insol.	$0.0068^{18°}$
Perchlorate	...	(No ppt.)	Sol.
Periodate	...	(No ppt.)	Insol.
Phosphate (dibasic)	Insol.	Insol.	1.4×10^{-5} $^{20°}$
Sulfate	$19^{19°}$	Sol. (1)	2.8×10^{-3} $^{0°}$
Sulfide	2×10^{-6} $^{18°}$	Insol.	Insol.
Sulfite	...	(No ppt.)	Insol.
Thiocyanate	Sol.	Sol.	$0.05^{20°}$
Tungstate	Insol.	Insol.	Insol.
Vanadate	...	Insol.	...
Succinate	...	Insol.	...

[a] Cahours, *Ann.*, **114**, 367 (1860). [b] E. Krause, *Ber.*, **51**, 1447 (1918). [c] Gmelin–Kraut's *Handbuch der anorg. Chemie*, 7 Ed., Vol. IV, Part 1, Carl Winter's Universitätsbuchhandlung, Heidelberg, 1911, pp. 285–373. [d] "Lange's Handbook of Chemistry," 6th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, pp. 259–260 (Sn. cpds.); pp. 206–210 (Pb cpds.). [e] SnF_2 forms complexes of the type M_2SnF_4 and $MSnF_3$; *cf.* M. E. Fremy, *Ann. chim. phys.*, **47**, [3], 1 (1856). R. Wagner, *Ber.*, **19**, 896 (1886). Me_2SnF_2 is soluble in KF soln. to give complexes of the type $K_2[(CH_3)_2SnF_4]$ (note *b* above). [f] $SnCl_2$ forms addition cpds. (or double salts) with amine hydrochlorides: *cf.* note *c*, p. 342. Me_2SnCl_2 forms double salts of this kind also: $Me_2SnCl_2{\cdot}2C_5H_5N{\cdot}HCl$ and others *cf.* P. Pfeiffer, *Z. anorg. Chem.*, **71**, 97 (1911). P. Pfeiffer, *Ann.*, **376**, 310 (1910).

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CAMBRIDGE, MASSACHUSETTS

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[10] If the supposition of ionization of the 5 p^2 electrons is correct, the anhydrous $(CH_3)_2Sn^{++}$ ion should be linear. An investigation of the structure of this cation in typical salts is in progress.

[11] H. M. Powell and D. M. Crowfoot, *Z. Krist.*, **87**, 370 (1934), found that dialkylthallium compounds have linear R_2Tl groups which are placed in such a way that the hydrocarbon groups are between the Tl x planes.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XVII. Heat Capacity of Titanium from 15 to 305°K.[1]

BY CHARLES W. KOTHEN AND HERRICK L. JOHNSTON

RECEIVED MARCH 30, 1953

The heat capacities of titanium have been measured in the temperature range 15 to 305° K., and the derived thermal functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16° K. is 7.33 ± 0.02 e. u.

Introduction

Low temperature heat capacity measurements on titanium have been made by Kelley[2] between 53 and 295°K., but his sample contained over 1% of impurities. The titanium used in the present research was of much greater purity than Kelley's and hence the thermal data reported should be more accurate.

Apparatus and Materials

The sample of iodide-process titanium was generously donated by the New Jersey Zinc Co., Palmerton, Pa. The principal contaminants were 0.0082% Mn, 0.007% Si and 0.0066% Al, with a total of 0.02% of N, Te, Pb and Cu. The rough rod was cut into small pieces on a shaper and these pieces were annealed in a high vacuum at 800°.

"Solid Calorimeter No. 3," one of the group of seven vacuum calorimeters described in the first paper of this series,[3] was used for the heat capacity measurements on 121.656 g. (2.5481 g. atoms) of titanium.

Experimental Results and Calculations

The experimental heat capacity data are presented in Table I. These deviate from a smooth curve by an average of 0.2 of 1%. Skinner[4] noticed that his data on zirconium were higher than Todd's[5] data below 130°K. and lower than Todd's data above 130°K. The discrepancy was attributed to oxygen in Todd's sample. The present data show a similar discrepancy with Kelley's data, the tem-

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[1] This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

[3] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

[4] G. B. Skinner and H. L. Johnston, *ibid.*, **73**, 4549 (1951).

[5] S. S. Todd, *ibid.*, **72**, 2914 (1950).

TABLE I

HEAT CAPACITY OF TITANIUM

At. wt. = 47.90 g., 2.5481 g. atoms

Mean T, °K.	C_p, cal./deg./g. atom	Mean T, °K.	C_p, cal./deg./g. atom
15.44	0.046	94.76	3.252
17.36	.056	104.49	3.583
18.75	.067	114.76	3.887
20.04	.081	127.07	4.215
21.31	.090	137.65	4.439
22.87	.117	148.70	4.654
24.60	.149	160.37	4.855
26.71	.192	172.74	5.020
29.32	.260	185.70	5.161
32.23	.349	198.46	5.305
35.26	.456	212.40	5.427
38.67	.590	215.29	5.466
43.54	.808	224.52	5.536
49.04	1.085	234.03	5.602
53.89	1.350	248.05	5.682
58.00	1.572	259.30	5.768
59.33	1.653	271.73	5.865
63.95	1.873	283.32	5.913
70.27	2.173	293.57	5.950
77.00	2.489	299.58	5.958
85.62	2.880	305.51	6.005

perature of intersection of the two heat capacity curves being about 180°K., and again the reason seems to be due to the contaminants in Kelley's titanium.

The heat capacity and derived thermal functions for titanium at integral values of the temperature are presented in Table II. The entropy at 298.16°K. is 7.33 ± 0.02 e.u. of which only 0.13 e.u. was obtained by extrapolation by the Debye T^3 law. This compares with the value 7.24 e.u. obtained by Kelley.[2]

TABLE II

THERMODYNAMIC FUNCTIONS OF TITANIUM

Temp., °K.	C_p^0, cal./deg./g. atom.	S^0, cal./deg./g. atom	$H^0 - H_0^0$, cal./deg./g. atom	$-(F^0 - H_0^0)/T$, cal./deg./g. atom
15	0.040	0.013	0.15	0.003
25	0.157	.054	0.94	.017
50	1.136	.414	15.31	.108
75	2.402	1.123	50.1	.322
100	3.434	1.963	133.7	.626
125	4.155	2.811	229.0	.979
150	4.684	3.652	339.9	1.386
175	5.043	4.403	461.9	1.764
200	5.321	5.095	591.5	2.137
225	5.539	5.735	727.3	2.502
250	5.713	6.328	868.0	2.856
275	5.864	6.879	1012.8	3.196
298.16	5.976	7.334	1149.9	3.478

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CARNEGIE INSTITUTE OF TECHNOLOGY, DEPARTMENT OF CHEMISTRY]

The Heat of Formation of Beryllium Oxide[1]

BY LEE A. COSGROVE AND PAUL E. SNYDER

RECEIVED DECEMBER 31, 1952

The heat of formation of beryllium oxide has been redetermined by means of the precision oxygen bomb calorimeter. The material burned consisted of high purity foil about two mils thick. Because of the high temperatures involved, the combustion was performed in beryllia crucibles. The results of this investigation yielded a value of −143.1 ± 0.1 kcal./mole for the standard heat of formation of the above compound.

A survey of the literature for values of the heat of formation of BeO showed the usual abundance of values with a range from approximately 131 to 152 kcal./mole of compound. These are listed in Table I. In this table the second, fourth, sixth, eighth and ninth values were obtained by use of the bomb calorimeter. The first, third and fifth values were obtained by solution in HF. Unfortunately, as is usually the case with older work in this field, little attention has been paid to such details as impurities and corrections. Furthermore, metal combustions have been carried out using ignition aids of various kinds. It is felt that, of the values shown, only that of Neuman and co-workers obtained in 1934 and the 1938 value of Roth deserve serious consideration. However, since the other values cannot be completely ignored without further evidence, it was considered proper to make another determination of the standard heat of formation of BeO in order to attempt to clear up the uncertainty.

TABLE I

Investigators	Date	$-\Delta H$, kcal./mole
Copaux and Philips[2]	1920	151.5
Mielenz and Wartenburg[3]	1921	135.9
Copaux and Philipps[4]	1923	131.1
Moose and Parr[5]	1924	134.2
Matignon and Marchal[6]	1926	137.4
Roth and Becker[7]	1929	135
Roth and Bückner[7]	1929	137.6
Newman, Kröger and Kunz[8]	1934	145.3 ± 0.2
Roth and Börger[9]	1937	138
Roth, Börger and Siemonsen[7]	1938	147.3 ± 0.6
This work	1951	143.1 ± 0.1

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[1] This work was performed under contract with the Office of Naval Research.

(2) H. Copaux and C. Phillips, *Compt. rend.*, **171**, 630 (1920).

(3) W. Mielenz and H. von Wartenburg, *Z. anorg. allgem. Chem.*, **116**, 267 (1921).

(4) H. Copaux and C. Phillips, *Comp. rend.*, **176**, 579 (1923).

(5) J. Moose and S. Parr, THIS JOURNAL, **46**, 2656 (1924).

(6) C. Matignon and G. Marchal, *Compt. rend.*, **183**, 927 (1926).

(7) W. Roth, E. Börger and H. Siemonsen, *Z. anorg. allgem. Chem.*, **239**, 321 (1938).

(8) B. Newman, C. Kröger and H. Kunz, *ibid.*, **218**, 379 (1934).

(9) W. Roth and E. Börger, *Ber.*, **70B**, 48 (1937).