TABLE I

ORGANOTIN COMPOUNDS PREPARED BY THE DIAZOMETHANE METHOD TOGETHER WITH SOME OF THEIR DERIVATIVES

Compound	Yield, %	B.p. °C.	B.p. Mm.	n^{25}_{D}	d^{25}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Other, % Calcd.	Other, % Found
$(CH_3)_2(CH_2Cl)SnCl$	70–80	76.7	11	1.5263		15.42	14.97	3.45	3.35		
$(CH_3)_2(CH_2Br)SnBr$	73	75–79	3.5–4	1.5683		11.17	11.72	2.50	2.66		
$(CH_3)_2(CH_2I)SnI$	78	111–111.2	5	1.6690		8.6	8.76	1.92	1.98		
$(CH_3)_2(CH_2I)SnF$	..	*d*				11.67	11.24	2.61	2.93	38.45	38.78[a]
$(n\text{-}C_4H_9)_2(CH_2Cl)SnCl$	74.5	106–110	0.3	1.5095	1.378	33.9	34.01	6.32	6.30		
$m\text{-}C_4H_9(CH_2Cl)_2SnCl$	57.9	82–87	0.18–0.2	1.5394	1.649	23.22	23.34	4.22	4.21	38.26	38.06[a]
$(C_6H_5)_2(CH_2Br)SnF$	..	*e*				40.50	41.66	3.14	3.37		
$(CH_3)_3SnCH_2Cl$	73	44–48	15	1.4860	1.556	22.52	22.65	5.20	5.35	16.62	17.61[b]
$(CH_3)_3SnCH_2Br$	71	46.2–50	11	1.5070	1.722	18.64	18.79	4.30	4.42		
$(CH_3)_3SnCH_2I$	78	53–54.5	6.5	1.5510		15.78	15.92	3.65	3.70		
$(n\text{-}C_4H_9)_3SnCH_2Cl$	80	108–112	0.5	1.4801	1.135	45.99	47.03	8.61	8.89[c]		
$(CH_3)_3SnCH_2SCN$	69	104–105	4	1.5247	1.491	25.45	25.52	4.70	4.81		

[a] Tin. [b] Chlorine. [c] Repeated fractionation did not improve the C, H values. [d] Dec. ~290°. [e] M.p. >260°.

iodide dissolved in 100 ml. of anhydrous acetone. Sodium chloride precipitated immediately. The mixture was refluxed for 22 hours, cooled and filtered. Distillation of the acetone at atmospheric pressure and fractionation of the residue gave 16.6 g. of iodomethyltrimethyltin, a yield of 78%. The product, originally colorless, changed to yellow in color on standing in daylight and the odor of a trialkyltin halide became apparent. Carbon–tin bond cleavage by the liberated iodine is thus indicated.

6. **Thiocyanomethyltrimethyltin.**—To a hot solution of 5.7 g. (0.7 mole) of sodium thiocyanate in 36 ml. of 95% ethanol was added 6.1 g. (0.0285 mole) of chloromethyltrimethyltin and 10.7 g. (0.0415 mole) of bromomethyltrimethyltin. Sodium halide precipitated immediately. After the mixture had been shaken intermittently for two hours it was filtered. The filtrate was shaken with twice its volume of distilled water and the organic layer was separated. The aqueous layer was extracted twice with ether. After drying of the combined organic layer and ether extracts the ether was removed by distillation and the residue was fractionated to give 11.4 g. of thiocyanomethyltrimethyltin. The originally colorless product turned red on standing in a stoppered vial in the dark.

This method also was successfully applied to the preparation of organotin compounds in which the thiocyanate group is linked to the tin atom. Dimethyltin dithiocyanate and di-*n*-butyltin dithiocyanate were prepared from the respective chlorides in this manner in good yield. In these preparations the filtrate was not washed with water, but was evaporated to leave the crude, crystalline thiocyanates which were purified by recrystallization. Dimethyltin dithiocyanate $(CH_3)_2Sn(SCN)_2$, fine white needles from benzene, m.p. 198.6–199.4° (dec. to a red liquid). *Anal.* Calcd. for $C_4H_6S_2N_2Sn$: C, 18.15; H, 2.28. Found: C, 18.31; H, 2.50. Dibutyltin dithiocyanate $(n\text{-}C_4H_9)_2Sn(SCN)_2$, fine white needles from chloroform, m.p. 144–145°. *Anal.* Calcd. for $C_{10}H_{18}S_2N_2Sn$: Sn, 34.00. Found: Sn, 34.02.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The Low Temperature Heat Capacity and Entropy of Cadmium Iodide

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The heat capacity of crystalline cadmium iodide has been measured between 15 and 300°K. At 298.16°K. C_p = 19.11 cal./mole deg. and S^0 = 38.5$_0$ e.u. of which 1.5 e.u. has been obtained by extrapolation below 15°K. Heat capacity, entropy and certain derived thermodynamic quantities are tabulated at 10° intervals up to 300°K. The heat capacity of cadmium iodide rises so rapidly at very low temperatures that near 15°K. it varies approximately as $T^{1.4}$. Nowhere above 15°K. does the heat capacity follow either the Debye T^3 law or the T^2 relationship shown by certain substances which have layer lattice structure.

A number of recent studies of crystalline substances with so-called "layer structure" have shown that, where this structure is sufficiently pronounced, the heat capacity follows a T^2 dependence and does not follow the usual Debye T^3 law in the approximate range 15 to 60°K. Thus, graphite,[1] gallium[2] and boron nitride[3] have been shown to obey the T^2 relationship and suggestions have been made[4] concerning similar behavior in other compounds.

Crystalline cadmium iodide, CdI_2, has a so-called "layer structure"[5] but with less marked anisotropy than is the case with graphite or boron nitride. The iodines form a nearly perfect hexagonal close packed array with cadmiums occupying octahedral holes of alternate layers, so that the lattice of cadmium iodide is rather like a stack of sandwiches. Thus, it was of considerable interest to learn whether cadmium iodide is sufficiently layer-like to cause the low-temperature heat capacity to follow a T^2 dependence. Furthermore, we were interested in determining thermodynamic constants

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(1) W. DeSorbo and W. W. Tyler, *Phys. Rev.*, **83**, 878 (1951); *J. Chem. Phys.*, **21**, 1660 (1953).

(2) W. DeSorbo, *ibid.*, **21**, 168 (1953).

(3) A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *ibid.*, **21**, 954 (1953); **22**, 837 (1954).

(4) V. V. Tarassov, *Compt. rend. acad. sci. U.R.S.S.*, **46**, 20, 110 (1945); **54**, 795 (1946); *Doklady Akad. Nauk U.R.S.S.*, **58**, 577 (1947); *Zhur. Fiz. Khim.*, **24**, 111 (1950).

(5) See, for example, R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers Inc., New York, N. Y., 1948, Chap. IV, text, p. 9; table, p. 19; Fig. 6; or A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, pp. 101 and 145.

for this substance in connection with fundamental studies of salts which complex readily.

Experimental

Materials.—J. T. Baker Chemical Company, C.P. Analyzed cadmium iodide was used. Two samples were prepared from this material. Sample a was dried in an oven for 20 hours at 115°, cooled in a desiccator and loaded directly into the calorimeter can in a dry-box. Sample **b** was placed on a high vacuum line and pumped for about a week after which its temperature was raised by a furnace and it was maintained under high vacuum at 150 to 170° for an additional ten days with occasional purgings by dry helium. Following this, sample **b** was sealed off under high vacuum, cooled, opened in a dry-box and charged at once into the calorimeter can. This drastic treatment was used in an attempt to remove any volatile impurities, particularly traces of moisture or organic solvents.

Calorimeter and Cryostat.—A low temperature, adiabatic calorimeter and cryostat were used which have been described by Oliver and Grisard[6] and by the present authors.[3] No essential changes were made from the description given by us. The calorie equal to 4.1840 absolute joules was used in converting electrical to thermal energy. The temperature scale was established with a calorimetric type platinum resistance thermometer which had been calibrated from 10°K. to 500°C. by the National Bureau of Standards.

The calorimeter can, including thermometer and heater, weighed 56.3984 g. and was calibrated as described previously.[3] After calibration the can was charged with 124.3034 g. (*in vacuo*) of cadmium iodide and following evacuation about 3 mm. of helium at room temperature was admitted.

The over-all accuracy of C_p measurements should be better than 0.2% above 50°K. and not less than 0.5% at 15°K.[6]

The formula weight of cadmium iodide is equal to 366.23 (1952 atomic weights).

TABLE I

RAW DATA—HEAT CAPACITY OF CdI_2

Temp., °K.	C_p, cal./mole deg.	Temp., °K.	C_p, cal./mole deg.	Temp., °K.	C_p, cal./mole deg.
16.08	2.758	115.17	16.696	271.71	18.880
20.24	3.975	120.54	16.844	277.96	18.924
25.05	5.466	126.95	16.999	285.30	19.008
29.33	6.830	133.55	17.160	293.73	19.006
34.37	8.293	140.87	17.324	302.12	19.180
40.08	9.762	148.06	17.454	247.39	18.556
46.40	11.111	155.15	17.578	256.01	18.650
		161.30	17.680	264.58	18.857
18.97	3.639	168.23	17.774	273.51	18.939
23.31	4.926			281.92	18.966
29.10	6.572	133.60	17.145	290.30	19.036
35.32	8.525	140.92	17.347	298.65	19.076
40.60	9.808	148.11	17.451		
46.54	11.149	155.20	17.557	209.26	18.242
52.77	12.298	161.55	17.664	215.78	18.277
		168.48	17.748	222.27	18.335
		175.33	17.866	228.73	18.357
54.13	12.543	182.12	17.934	235.15	18.432
58.35	13.173	188.85	18.036	241.54	18.492
63.43	13.780	195.52	18.100	247.90	18.520
69.46	14.255	202.15	18.181	254.23	18.523
76.38	14.826	208.73	18.211	260.52	18.631
82.89	15.324	215.28	18.224	261.10	18.688
		221.79	18.286	267.34	19.116
				273.54	18.879
54.20	12.519	177.10	17.881	279.75	18.970
59.61	13.359	183.88	17.980	285.94	19.016
65.91	13.987	190.61	18.059	292.11	19.064
73.10	14.558	197.29	18.113	298.24	19.061
79.82	15.080	202.52	18.140		
86.18	15.530	211.49	18.222	260.21	18.651
92.27	15.860	220.38	18.305	266.52	18.878
		229.21	18.379	258.77	18.580
89.73	15.778	237.97	18.446	264.08	18.627
95.72	15.949	246.67	18.540	268.40	18.963
101.53	16.201	252.51	18.578	272.69	18.863
107.18	16.425	261.13	18.679	264.82	18.760
113.84	16.641	269.66	19.023	267.13	19.078
121.57	16.843			269.41	19.400
129.12	17.041			271.70	18.822
109.69	16.494	259.11	18.631	274.01	18.937
		265.43	18.824	276.32	18.875

Results and Discussion

The raw heat capacity (C_p) data for one mole of cadmium iodide (sample **a**) are given in Table I, where T_m is the mean temperature of an individual heat capacity measurement and the magnitude of the temperature rise can be gaged from successive T_m values. All measurements were taken in the order recorded, with ten individual series being made. A plot of the data is shown in Fig. 1. Smoothed values of heat capacity, entropy and the functions $-(F^0 - H_0^0)/T$ and $(H^0 - H_0^0)/T$ have been obtained by standard graphical methods and are recorded in Table II.

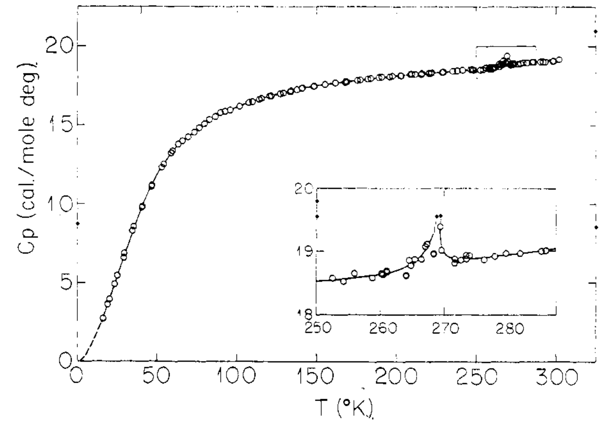

Fig. 1.—Heat capacity of cadmium iodide.

A very small peak was observed in the heat capacity curve at 269.5°K. which has the general shape and appearance of a lambda transition. The shape of this transition is shown in the inset of Fig. 1, while its small size is evident from the complete curve. Repeated measurements through this transition range showed that the peak was reproducible and that whatever phenomenon causes it is reversible within the time required to cool the sample and calorimeter 30 or 40° below 269.5°K. The area under the peak amounts to no more than 3 cal./mole and the associated entropy is about 0.01 e.u. An explanation for the peak is not obvious. The possibility exists that traces of water might cause such an effect if some of the cadmium iodide were to dissolve in the water, thereby lowering its freezing point (melting point). The difference between the freezing point of pure water and 269.5°K. is a reasonable amount on this basis. However, the shape of the peak does not seem to support the idea of a melting point depression. Some small transition in cadmium iodide is entirely possible,

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(6) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

TABLE II

SMOOTHED MOLAR THERMODYNAMIC FUNCTIONS OF CdI_2

Temp., °K.	C_p, cal./mole deg.	S^0, e.u.	$-\frac{(F^0 - H_0^0)}{T}$, cal./mole deg.	$\frac{(H^0 - H_0^0)}{T}$ cal./mole deg.
10	...	0.60	0.26	0.34
20	3.93	2.22	0.83	1.39
30	6.99	4.39	1.66	2.73
40	9.74	6.79	2.64	4.15
50	11.84	9.19	3.70	5.49
60	13.33	11.51	4.82	6.69
70	14.33	13.65	5.93	7.72
80	15.10	15.61	7.02	8.59
90	15.72	17.43	8.08	9.35
100	16.17	19.11	9.10	10.01
110	16.53	20.67	10.08	10.59
120	16.82	22.12	11.03	11.09
130	17.07	23.48	11.93	11.55
140	17.29	24.75	12.81	11.94
150	17.48	25.95	13.64	12.31
160	17.65	27.09	14.45	12.64
170	17.80	28.16	15.23	12.93
180	17.92	29.18	15.98	13.20
190	18.05	30.15	16.70	13.45
200	18.14	31.08	17.39	13.69
210	18.22	31.97	18.07	13.90
220	18.30	32.82	18.72	14.10
230	18.39	33.64	19.35	14.29
240	18.48	34.42	19.96	14.46
250	18.54	35.18	20.55	14.63
260	18.65	35.91	21.13	14.78
262	18.69			
265	18.84			
268	19.21			
269.6	19.67			
270	18.86	36.62	21.69	14.93
273.16	18.87	36.84	21.86	14.98
280	18.94	37.31	22.24	15.07
290	19.03	37.98	22.77	15.21
298.16	19.11	38.50	23.19	15.31
300	19.12	38.62	23.29	15.33

but it seems unlikely that it should be of so small a magnitude as the peak reported here. In order to check the possibility that water or some other adsorbed volatile impurity might be responsible for the observed effect, the heat capacity of a second sample of cadmium iodide (sample **b**), outgassed and dried as described above, was measured between 250 and 280°K. A reversible peak of the same size and shape observed with sample **a** was again found at 269.5°K. in confirmation of the data presented in Table I. The measurements with sample **b** were taken for confirmation of the peak only and the calorimeter can was not matched exactly with the calibration run, so the data are not included in Table I since the heat capacities with this sample are not comparable to closer than about one per cent. with those of Table I. However, these results do give strong indication that the peak at 269.5°K. is not the result of adsorbed moisture or organic solvent, since any such material should have been removed by the treatment given sample **b**. We are unable to give any satisfactory explanation of the peak. It is evident that the magnitude of this heat capacity effect and the associated entropy is practically negligible in arriving at the thermodynamic quantities recorded in Table II.

Figure 1 shows that the heat capacity of cadmium iodide rises rapidly in the very low temperature range so that at 15°K. (C_p = 2.5 cal./mole deg.) it amounts to a sizeable proportion of the so-called "classical" high temperature heat capacity of 18 or 19 cal./mole deg. As a result, the temperature dependence of the heat capacity in the range from 15 to 50°K. follows neither the customary Debye T^3 law nor the T^2 relation observed with certain substances having layer-lattices. A plot of log C_p *vs.* log T shows that at the lowest temperature studied C_p varies as about $T^{1.4}$. It is of considerable interest to learn how C_p will vary at still lower temperatures and we plan to investigate this problem in the near future.

Although no simple temperature dependence can be used to extrapolate the heat capacity of cadmium iodide to absolute zero, we believe that the graphical extrapolation which we have followed leaves little uncertainty in the derived thermodynamic quantities,[7] barring the existence of some major transition below 15°K. which seems unlikely. We may note that Bates[8] used electromotive force measurements to arrive at the value of 39.5 ± 1.0 e.u. for the entropy of cadmium iodide at 25° which is to be compared with our calorimetric value of 38.5 e.u.

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(7) Although graphical extrapolation strictly according to the average values between 30 and 16°K. results in entropy larger than given in Table II, T^3 extrapolation results in lower values. We have chosen an extrapolation approximately midway between these two extremes. The difference between our extrapolation and one based on the average slope between 30 and 16°K. is 0.49 e.u.; however, it appears from a large scale plot that this latter extrapolation gives much too large an entropy. We feel that our method is probably reliable to 0.3 e.u.

(8) R. G. Bates, THIS JOURNAL, **61**, 1040 (1949).