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The Thermodynamic Properties of Cadmium Dimethyl: Heat Capacities from 14 to 291°K., Heats of Transition, Fusion and Vaporization, Vapor Pressure up to 296°K. and the Entropy of Ideal Gas

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The heat capacities of both solid and liquid cadmium dimethyl have been measured from 14 to 291°K. A sharp transition at 254.35 ± 0.05°K. has been observed with a heat of transition of 363.5 ± 0.5 cal./mole. The melting point is found to be 270.48 ± 0.05°K. and the heat of fusion 1873 ± 1 cal./mole. The vapor pressure has been measured from the melting point to 296°K. and also the heat of vaporization at 291.5°K. which is found to be 9153 ± 30 cal./mole. The entropy of the liquid and the ideal gas have been calculated to be 48.25 ± 0.10 and 72.40 ± 0.20 cal./mole deg., respectively, at 298.16°K. and 1 atm. The value of the ideal gas is compared with the result from molecular data and agreement is obtained on the basis of free internal rotation.

This report presents the results of a low temperature calorimetric investigation on cadmium dimethyl. The purpose was to determine the entropy of the ideal gas from the third law of thermodynamics and to compare it with the result calculated from molecular data. There is particular interest in the potential barrier hindering internal rotation of the two methyl groups with respect to each other since the methyl–methyl separation in this molecule is between those of ethane and dimethylacetylene.

The results are presented in terms of the defined thermochemical calorie; the ice point is taken as 273.16°K.

The Purity and the Melting Point.—The sample of cadmium dimethyl was prepared by Dr. R. L. Williams in this Laboratory. It had been sealed in a glass container painted black. After about three months, the liquid looked slightly cloudy. When it was carefully distilled into the calorimeter, some traces of white residue remained on the wall of the container. However, the measurement of melting points showed that the sample was still very pure, as seen from Table I where the first figure was obtained from premelting heat capacities. The amount of liquid soluble–solid insoluble impurity was calculated to be less than 0.01%. The melting point was 270.48 ± 0.05°K. or −2.68 ± 0.05°. A value of −2.4° has been reported by Anderson and Taylor.[1] Their technique seems to be less accurate than ours and the difference is probably within the experimental error of their cooling curve extrapolation.

TABLE I

MELTING POINT OF $Cd(CH_3)_2$

Fraction melted	Temp., °K.	Fraction melted	Temp., °K.
0.002	268.31	0.30	270.47
.05	270.38	.48	270.47
.13	270.44	.73	270.48
.22	270.46	.87	270.48

The Heat Capacities.—The method of low temperature heat capacity measurement has been described in the literature.[2] The calorimeter used was the same one employed for the study of 1,1-dichloroethane.[3] Some small changes in the resistance thermometer were observed and therefore a new R–T table was constructed and smoothed to the second differences.

The actual observed heat capacities, with no correction for premelting or transition, are listed in Table II and the smoothed values in Table III where a correction is made for premelting. No abnormal phenomenon was observed around the transition. The ΔT used for each heat capacity measurement is about 10% of the absolute temperature below 60°K. Above 60°K., the ΔT is six to seven degrees except those within six degrees before melting where ΔT is about 1.5 to 2°. The smoothed heat capacities are believed to represent true values to 0.1–0.2% above 50°K., 0.5% from 20 to 50°K. and about 1% below 20°K.

TABLE II

EXPERIMENTAL HEAT CAPACITIES OF $Cd(CH_3)_2$

Temp., °K.	C_p, cal./mole deg.
Solid II	
14.13	1.87
15.59	2.26
16.96	2.58
17.31	2.72
19.40	3.18
21.94	3.82
24.56	4.34
27.97	5.03
33.06	6.08
36.90	6.97
40.75	7.83
44.76	8.61
49.64	9.53
54.88	10.53
60.34	11.52
66.13	12.46
71.89	13.28
74.87	13.62
78.18	14.06
79.57	14.26
84.90	14.87
90.89	15.42
96.83	16.02
100.99	16.29
107.14	16.85
112.85	17.27
118.77	17.72
124.74	18.13
130.66	18.50
136.56	18.92
141.75	19.19
147.81	19.55
154.39	19.94
160.64	20.30
167.30	20.69
174.38	21.04
181.06	21.47
187.50	21.88
193.74	22.24
200.95	22.61
207.91	22.98
214.57	23.35
221.56	23.71
228.81	23.90
235.79	24.31
236.48	24.36
242.26	24.65
246.66	24.89
248.38	24.95
250.26	25.04
Solid I	
257.50	24.57
258.65	24.70
259.26	24.84
260.16	24.86
261.92	25.01
261.95	24.97
263.26	25.08
263.77	25.23
265.43	25.50
265.61	25.68
267.19	26.71
268.81	33.14
Liquid	
278.87	31.31
279.06	31.27
284.97	31.40
287.54	31.44
291.33	31.45

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[1] R. D. Anderson and H. A. Taylor, *J. Phys. Chem.*, **56**, 161 (1952).

[2] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[3] J. C. M. Li and K. S. Pitzer, THIS JOURNAL, **78**, 1077 (1956).

TABLE III

SMOOTHED HEAT CAPACITIES OF $Cd(CH_3)_2$

Temp., °K.	C_p, cal./mole deg.	Temp., °K.	C_p, cal./mole deg.
15	2.10	160	20.26
20	3.36	170	20.83
25	4.42	180	21.42
30	5.44	190	22.00
35	6.53	200	22.56
40	7.64	210	23.08
45	8.65	220	23.56
50	9.62	230	24.04
55	10.56	240	24.53
60	11.46	250	25.05
65	12.29	254.35	25.27
70	13.03	Transition	
80	14.30	254.35	24.30
90	15.36	260	24.81
100	16.27	270[a]	25.73
110	17.07	270.48[a]	25.77
120	17.81	Fusion	
130	18.47	270.48	31.11
140	19.10	280	31.31
150	19.68	290	31.47
		300	31.57

[a] Corrected for premelting.

Vapor Pressure.—The method of vapor pressure measurement was the same as in the previous investigation.[3] The results were reduced to international cm. of mercury at 0° and standard acceleration of gravity. They are shown in Table IV together with the difference from the calculated values using the equation

$$\log_{10} p_{\text{cm}} = 24.6096 - \frac{2759}{T} - 6 \log T$$

TABLE IV

VAPOR PRESSURE OF $Cd(CH_3)_2$

Temp., °K.	p_{obsd}, cm.	$p_{\text{obsd}} - p_{\text{calcd}}$, cm.	Temp., °K.	p_{obsd}, cm.	$p_{\text{obsd}} - p_{\text{calcd}}$, cm.
270.48	0.650	−0.005	290.80	2.183	−0.007
278.98	1.113	.000	291.82	2.314	.000
281.68	1.313	+ .006	291.83	2.317	+ .001
284.67	1.560	+ .005	292.01	2.331	− .007
285.75	1.661	+ .007	294.41	2.664	+ .006
287.15	1.792	+ .003	295.96	2.886	+ .002
289.56	2.046	.000			

The vapor pressures up to the boiling point have been measured by Bamford, Levi and Newitt[4] and by Anderson and Taylor.[1] The former series was relatively crude and the sample used was believed to be impure (m.p. −4.2°). The latter series differs with the results of this work only by a uniform amount of about 1 mm. which is considered to be within the accuracy of their technique.

Heats of Transition, Fusion and Vaporization.—The heats of transition, fusion and vaporization were measured in the usual manner[3] and the results are presented in Tables V, VI and VII. They are, respectively, 363.5 ± 0.5, 1873 ± 1 and 9153 ± 30 (291.5°K.) cal./mole. The temperature of transition (254.35°K.) was determined at various extents of transition and no change was observed.

Because of the low vapor pressure, the capillary, which had been used before[3] for vaporization measurements, was not used in this case. The temperature control was relatively difficult as seen from the large temperature variation in Table VII. Another uncertainty which might result from the absence of the capillary was in the temperature of vaporization. However, all these effects were considered to introduce less than 30 cal./mole uncertainty in the final values.

TABLE V

HEAT OF TRANSITION OF $Cd(CH_3)_2$

Initial and final temp., °K.	Heat input, cal./mole	Heat of transition, cal./mole
252.52 to 257.66	546.4	363.4
251.62 to 257.36	568.2	363.5
253.01 to 258.30	551.5	363.6
253.95 to 256.64	458.5	363.4
	Av.	363.5 ± 0.5

TABLE VI

HEAT OF FUSION OF $Cd(CH_3)_2$

Initial and final temp., °K.	Heat input, cal./mole	Heat of premelting, cal./mole	Heat of fusion, cal./mole
268.31 to 275.92	2178.3	4.1	1873.1
268.94 to 274.16	2076.5	8.0	1872.6
268.86 to 277.12	2205.1	7.3	1872.7
		Av.	1873 ± 1

TABLE VII

HEAT OF VAPORIZATION OF $Cd(CH_3)_2$

Amount vaporized, g.	Av. temp., °K.	Max. temp., variation	Heat of vaporization,[a] cal./mole
8.748	293.4	3.4	9130
11.988	291.5	1.1	9160
6.707	293.2	1.8	9170
		Av.	9153 ± 30
Calcd. from vapor pressure eq. of Anderson and Taylor[1]			9636
Calcd. from vapor pressure eq. of this work			9149

[a] Corrected to 291.5°K. by assuming ΔC_p = 12 cal./mole deg.

The heats of vaporization at 291.5°K. calculated from the vapor pressure equations of both this work and of Anderson and Taylor[1] are also listed in Table VII for comparison. The much too high value of Anderson and Taylor results probably partly from the uncertainty of their measurements and partly from the simplicity of the equation. On the other hand, the agreement between the other two values is rather accidental since the value obtained from vapor pressure measurements over such short range of temperature has at least 0.5% uncertainty.

The Entropy from the Third Law of Thermodynamics.—The extrapolation below 14°K. was obtained with the aid of a Debye function with four degrees of freedom. The resulting θ values were nearly constant in the range 14 to 20°K. and a value of 90° was selected for the calculation. The other portions of entropy were calculated by numerical integration of C_p/T against T using Simpson's rule. The portion from 14 to 50°K. was checked by numerical integration of C_p against log

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(4) C. H. Bamford, D. L. Levi and D. M. Newitt, *J. Chem. Soc.*, 468 (1946).

T. The vapor at 2 cm. pressure was assumed ideal. The third law entropy of the liquid and the ideal gas at 298.16°K. and 1 atm. were found to be 48.25 ± 0.10 and 72.40 ± 0.20 cal./mole deg., respectively. A summary of the calculation is shown in Table VIII.

TABLE VIII

CALCULATION OF ENTROPY OF $Cd(CH_3)_2$, CAL./MOLE DEG.

0 to 14°K. (θ = 90)	0.705
14 to 254.35°K. (solid II)	34.592
Transition 363.5/254.35	1.429
254.35 to 270.48°K. (solid I)	1.539
Fusion 1873/270.48	6.925
270.48 to 298.16°K. (liq.)	3.056
Liquid at 298.16°K.	48.246 ± 0.10
298.16 to 291.5°K.	−0.712
Vaporization 9153/291.5	31.400
Compression (2.275 cm. to 1 atm.)	−6.973
291.5 to 298.16°K. (C_p = 19.6)	0.442
Ideal gas at 298.16°K. and 1 atm.	72.40 ± 0.20

The Potential Barrier Hindering Internal Rotation.—A vibrational assignment has been made by Gutowsky[5] and is used for the calculation of vibrational contribution to the entropy except the band at 150 $cm.^{-1}$ which has been investigated again here by Dr. R. L. Williams. A band at 130 $cm.^{-1}$ was found in the infrared spectrum of the vapor and therefore used instead of 150 $cm.^{-1}$ in the calculation. The vibrational contribution thus calculated was 8.758 cal./mole deg. at 298.16°K. The moments of inertia were calculated by assuming C–Cd 2.15 Å., C–H 1.10 Å. and tetrahedral angles for HCH. The structure C–Cd–C was assumed linear. The product of moments of inertia thus found was 6.929×10^{-115} $g.^3$ $cm.^6$ and therefore the translational and over-all rotational contribution to the entropy was calculated to be 60.662 cal./mole deg. By comparison with the third law entropy of 72.40 ± 0.20 cal./mole deg. at 298.16°K. and 1 atm., the contribution due to internal rotation calculated by difference is 2.98 ± 0.20 cal./mole deg. If the internal rotation is free, the contribution calculated from the formula of Pitzer and Gwinn[6] using the reduced moment of inertia 2.70×10^{-40} g. $cm.^2$ is 2.925 cal./mole deg. Since the entropy can only decrease with restricted internal rotation, it can be concluded that the potential barrier hindering internal rotation is essentially zero. Since Dr. R. L. Williams' spectral studies may lead to further small changes in the vibration frequencies, it seems best to postpone the calculation of general tables of thermodynamic properties.

The conclusion of free internal rotation is in agreement with the spectroscopic work of Boyd, Williams and Thompson.[7]

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(5) H. S. Gutowsky, THIS JOURNAL, **71**, 3194 (1949).

(6) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(7) D. R. J. Boyd, R. L. Williams and H. W. Thompson, *Nature*, **167**, 766 (1951).

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Gadolinium–Hydrogen System[1]

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Pressure–temperature–composition data are presented for the gadolinium–hydrogen system. Two hydride phases exist, the first being a cubic structure of ideal composition close to GdH_2, the second being a hexagonal structure of ideal composition close to GdH_3. Both hydrides exist over composition ranges. A partial phase diagram and X-ray data for the Gd–H system are presented. An enthalpy change of −46.9 kcal. per mole of H_2 is obtained from the P–T–C data for the conversion of hydrogen-saturated gadolinium to hydrogen-deficient GdH_2 at temperatures from 600 to 800°.

Introduction.—The study of rare-earth hydrides is of interest to this Laboratory for two reasons. The first is simply the desire to add to the general store of fundamental knowledge concerning metallic hydrides. The second—more important to our immediate interests—is that the chemistry of the lanthanide elements has been very helpful as a basis for the study of the actinide elements because of similarities and analogies. The particular rare-earth hydride which is the subject of this article has proved to be a counterpart of plutonium hydride. The data presented here greatly strengthen deductions as to the phase relationships in the plutonium–hydrogen system, since it has not been possible to get unequivocal equilibrium data for plutonium hydride with high hydrogen content but such data have been obtained for Gd–H and are presented in this paper.

The only work previously published on gadolinium hydride has been by Viallard,[2] who claims that upon heating Gd in hydrogen to about 220°, Gd_2H_3 is formed which becomes GdH_2 upon cooling. Little evidence is presented to support this claim, however, and it seems probable to us that Viallard is mistaken about the existence of a hydride with formula Gd_2H_3.

This report presents pressure–temperature–com-

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) R. Viallard, *Compt. rend.*, **219**, 417 (1944).