Kopp–Neumann rule is linear with the alteration in composition, the correction of the specific heats from 50.52 to 50.00% will involve less than 0.05% error. This makes it appear that the specific heat behavior of MgCd can be computed from the results in Table II about as well as it can be measured. On this basis

$$C_p = \frac{C_p' - 0.0104(C_p)_{Cd}}{0.9896}$$

where

C_p = heat capacity of MgCd/g. atom

C_p' = heat capacity of alloy (50.52 atomic % Cd) per g. atom

From this

$$S = \frac{S' - 0.0104S_{Cd}}{0.9896}$$

where the subscripts and superscripts refer to the same materials as in the preceding equation

$$S' = 9.83 \text{ e.u./g. atom}$$
$$S_{Cd} = 12.37 \text{ e.u./g. atom}$$

from which

$$S = 9.80 \text{ e.u./g. atom}$$

Hence

$$S_{25°} - S_{0°K} = 9.80 \text{ e.u./g. atom of MgCd}$$

and

$$S_{0°K} = 0.15 \text{ e.u./g. atom}$$

Thus the residual entropy of MgCd obtained in this way significantly deviates from the requirements of the Third Law.

The Transformation between 230 and 300°K.

As previously indicated, the transformation occurred reversibly and over a considerable range of temperature. These features immediately suggested that it was a part of the order–disorder transition which destroys the MgCd ordered structure at 250°. This is the interpretation currently held, although initially there was some reluctance to accept the notion that atomic interchanges could occur at −40° with sufficient rapidity to produce the observed effects. The anomalous thermal behavior was noted fully 300° below the critical temperature, indicating what seemed to be an abnormally large width to the transition in view of the low temperatures involved.

The magnitude of C_v at the upper end of the temperature range covered in this paper and especially the agreement between the extrapolated C_v-curve and the heat capacity data obtained by Khomyakov, *et al.*,[19] between 25° and the critical point constitute convincing evidence that the low temperature transformation is the beginning of the disordering process. C_v at 25° is already above $3R$; this might be attributed to an electronic contribution, anharmonicity in the vibrations or a configurational effect. Of these the latter seems more plausible. There is nothing which would suggest an abnormally large electronic heat capacity in MgCd and at a temperature 400° below the melting point anharmonicity effects should be small. The smooth joining of the low and the high temperature C_p data means that the small excess heat capacity at 25° increases steadily to the critical point at 250°, where it becomes infinite. Resistometric and diffraction measurements confirm[12] the destruction of the ordered structure at this temperature. Near the order–disorder transition temperature the extra heat capacity is unmistakably configurational in origin, from which one can conclude that the anomalous heat capacity at 25° and the transformation which begins at 230°K. are indeed associated with the temperature variation of the degree of disorder.

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[CONTRIBUTION NO. 890 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Magnesium–Cadmium Alloys. VI. Heat Capacities between 12 and 320°K. and the Entropies at 25° of Magnesium and Cadmium[1,2]

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Constant pressure heat capacities of magnesium and cadmium are reported for temperatures between 12 and 320°K. From these data the entropies at 25° are found to be 7.78 ± 0.01 and 12.37 ± 0.01 e.u./g. atom for magnesium and cadmium, respectively. Constant volume heat capacities and Debye characteristic temperatures are also reported.

While determining the heat capacities of the MgCd superlattice, it was discovered that the heat capacities of the components were neither as complete nor as precise as desired. In this paper results of determinations of their low temperature heat capacities are presented along with calculations of their entropies at 25°.

Experimental

The apparatus and procedure were for the most part identical with those employed in studying MgCd. These have been described in the preceding paper[2] (hereinafter referred to as V). Measurements on cadmium were made first, using the equipment described in V. Results which seemed satisfactory were obtained below 150°K. but not at higher temperatures. The attainment of a constant temperature became increasingly slower above 150°K. presumably due to poor thermal conductivity of cadmium at the higher temperatures. It was feared that the results above 150°K. were systematically high due to the development of an excessive thermal head in the heater during the heating period, causing the loss of some heat along the lead wires. These experiments indicated the need for modifying the sample container to facilitate the distribution of heat.

Figure 1 shows the new sample container. It is to be noted that it more nearly resembles a conventional sample container in that it completely encloses the sample. Thus one can introduce helium gas to aid in the distribution of heat. The central tapered monel casing contains the plati-

(1) This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

(2) Reference to earlier papers in the series is given in the preceding paper by C. B. Satterthwaite, R. S. Craig and W. E. Wallace, THIS JOURNAL, **75**, 232 (1953).

num resistance thermometer and the heater. The bottom of the sample container is of stainless steel and is silver soldered to the monel casing and to the outer copper cylinder forming the outside of the container. A false bottom to hold the insulated binding posts for leads to the heater and thermometer is soldered onto the container below the stainless steel bottom. Leads are run from the heater and thermometer through an opening in the false bottom and around the sample container, the winding making good thermal contact through electrical insulating varnish. This winding acts as a thermal equilibration trap to prevent heat leakage along the leads during and immediately after a heating period when thermal lag allows the contents of the core to reach a higher temperature than the sample. The leads return through the same opening to the inside ends of the insulated binding posts.

A small bolt with a nut is provided on the side of the sample container for connection of one end of a difference thermocouple used in controlling the temperature of the adiabatic shield. The sides and top of the container are of copper and are gold plated to minimize heat exchange by radiation. The top is arranged to be soldered in place with Woods metal after inserting the sample. Final sealing of the container is accomplished by means of a tiny copper plug which can be quickly soldered into the tip of the previously tinned monel tube projecting from the top. The several new features which minimize heat loss along the leads are evident from this description.

Details of purity for the metals employed are given in V. Measurements were made on 127.589 g. or 5.2679 g. atoms of magnesium and on 641.990 g. or 5.7111 g. atoms of cadmium.

Experimental Results

Heat Capacities of Cadmium.—The smoothed results are given in Table I. They are based on experiments performed in six series of measurements: 12 to 65°K. (liquid helium cryostat), 65 to 211°K. (liquid air cryostat), 199–274, 209–259 and 270–294°K. (solid carbon dioxide cryostat) and 283 to 323°K. (ice cryostat). Measurements were made so as to cover the range from 12 to 320° K. completely. The thermal history of the sample was not carefully controlled, but in all cases the temperature was changed from that characteristic of the room to the working temperature in a time interval which was never less than an hour and usually 5 or more hours. Once a series of measurements was begun experiments were performed continuously until the series was concluded.

TABLE I

HEAT CAPACITIES OF CADMIUM AND MAGNESIUM

T, °K.	C_p,[a] cal./deg. g. atom Mag-nesium	Cad-mium	T, °K.	C_p,[a] cal./deg. g. atom Mag-nesium	Cad-mium
12	0.016	0.392	150	4.876	5.746
14	.026	.592	160	5.013	5.799
16	.042	.804	170	5.133	5.844
18	.065	1.020	180	5.236	5.884
20	.086	1.240	190	5.331	5.922
25	.188	1.803	200	5.418	5.956
30	.341	2.306	210	5.487	5.988
35	.550	2.760	220	5.550	6.018
40	.803	3.158	230	5.611	6.047
45	1.076	3.503	240	5.667	6.073
50	1.367	3.803	250	5.719	6.096
60	1.953	4.283	260	5.766	6.119
70	2.498	4.647	270	5.811	6.144
80	2.981	4.920	280	5.853	6.171
90	3.404	5.138	290	5.896	6.201
100	3.753	5.284	298.16	5.929	6.224
110	4.052	5.413	300	5.936	6.229
120	4.307	5.518	310	5.970	6.255
130	4.527	5.608	320	5.998	6.280
140	4.718	5.684			

[a] The calorie used is the "defined calorie" = 4.1840 absolute joules.

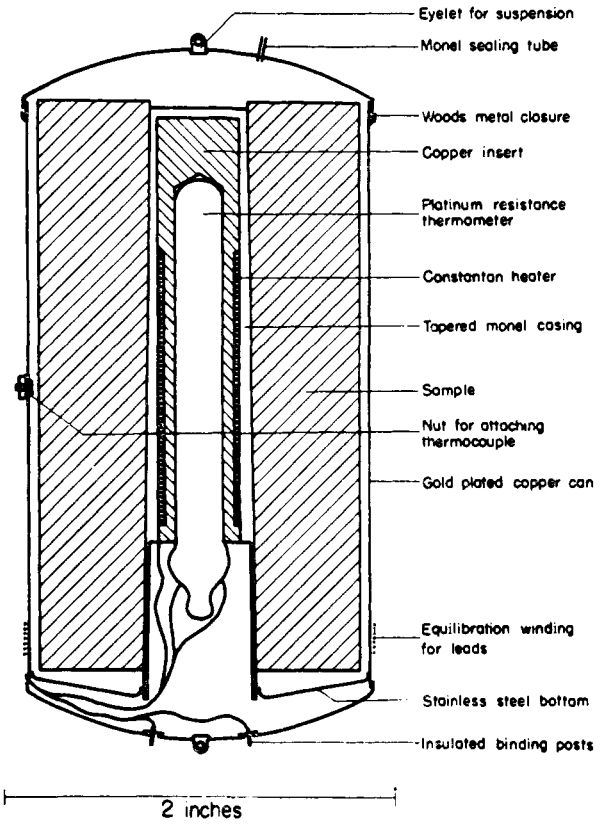

Fig. 1.—Sample container.

Results above 65°K. were obtained using the new sample container. These data were found to be lower by a maximum of 0.4% than those obtained with the original sample holder, as was expected if some heat were lost along the lead wires. The difference diminished with decreasing temperature and disappeared entirely in the liquid air region, where the original equipment behaved properly. The data reported for temperatures below 65°K. were obtained in the original series of determinations. From 70 to 240°K. the differences between the two sets of data were barely significant, but the second set seemed more reliable and only those data are reported.

Heat Capacities of Magnesium.—The smoothed results shown in Table I were obtained using the sample container shown in Fig. 1. These measurements were in all respects routine. Except for the facts that all data were taken with the new sample holder and the solid carbon dioxide range was covered in a single series of determinations, the procedure with magnesium was virtually identical with that for cadmium.

Entropies at 25°.—The entropy increment between absolute zero and 25° was obtained by graphical integration of the results in Table I, extrapolation below 12°K. being made by the T^3 law. Since these metals undoubtedly obey the Third Law, these are the absolute values at 25°.

Results are shown in Table II together with the values adopted in Kelley's compilation[3] and also Clusius and Vaughen's result for magnesium based on their heat capacity measurements.[4] The entropy of cadmium also was evaluated from the first set of data. This value was only 0.004 e.u./g. atom higher than that obtained from the data in Table I.

TABLE II

ENTROPIES OF MAGNESIUM AND CADMIUM AT 25°C.

Temp. interval, °K.	ΔS, e.u./g. atom Magnesium	Cadmium
12–298.16	7.77	12.24
0–12 (extrap.)	0.01	0.13
0–298.16	7.78	12.37
0–298.16 (Kelley)	7.77 ± 0.1	12.3 ± 0.1
0–298.16 (ref. 4)	7.76	

Precision of Experimental Quantities.—Average percentage deviations of the heat capacity determinations from a smooth curve were determined for several temperature ranges as in V. With magnesium these were 0.6, 0.2 and 0.03 in the temperature ranges 12–30, 30–70 and 70 to 320°K., respectively. The corresponding deviations for cadmium were 0.1, 0.01 and 0.02. These random errors introduce not more than 0.1% error in the entropies at 25°.

Comparison of Heat Capacities with Previous Determinations.—The heat capacities of cadmium have been determined previously by Lange and Simon[5] (10 to 300°K.), Rodebush[6] (69 to 298°K.) and Bronson and Wilson[7] (193 to 393°K.). Excellent agreement is found between the present results and those of Bronson and Wilson. In the 127° of overlap they agree within 0.07% on the average and the maximum deviation is 0.1%. Lange and Simon's data are lower than the data in Table I at temperatures below 30°K. by roughly 4%. Between 30 and 110°K. they exceed the present data. The difference is 2.6% at 50°K. and diminishes with increasing temperature to 0.4% at 110°K. At 120°K. the two sets of data are identical, but at higher temperatures Lange and Simon's results are consistently lower by an average of 0.3%. Rodebush's results exceed the data in Table I by an average of 0.5%.

Eastman and Rodebush[8] and Clusius and Vaughen[4] measured heat capacities of magnesium at low temperatures. Neither investigation appears to have been of high precision. The two sets of data disagree by up to 10% and both scatter appreciably about a smooth curve. A curve from Clusius and Vaughen's data crosses over the curve plotted in Table I at 5 points. C_p at 14°K. from Clusius and Vaughen's data is larger by 3.9% than that obtained in this study. The average deviations between the present results and those of Clusius and Vaughen at higher temperatures is as follows: +6% between 15 and 25°K., −2.5% between 25 and 60° K., +0.6% between 60 and 110°K., −0.3% between 110 and 180°K. and +0.8% between 180 and 220°K.

Heat Capacities at Constant Volume and the Debye Characteristic Temperatures.—Constant volume heat capacities for the two metals were computed at 25° from the data in Table I. For cadmium, the thermal expansivity (98.6×10^{-6} °C.$^{-1}$) was taken from paper IV of this series[9] and the compressibility was that given by Bridgeman[10] (2.07×10^{-6} atm.$^{-1}$). The corresponding quantities for magnesium were values from the "International Critical Tables": 7.68×10^{-5} (°C.)$^{-1}$ and 2.9×10^{-6} atm.$^{-1}$, respectively. Gram atomic volumes were obtained from densities reported earlier.[11] C_v values at lower temperatures were evaluated from the empirical expression $C_p - C_v = AC_p^2T$, with A being established from the 25° values of C_p and C_v. A was 3.81×10^{-5} for cadmium and 1.97×10^{-5} for magnesium, both in units of g. atom/cal. C_v's and Debye characteristic temperatures are given in Table III. The inconstancy of the Debye temperatures is particularly prominent in these two metals. It is well known that metallic cadmium has, because of its anomalous axial ratio, more complicated vibrational characteristics[12–14] than a normal hexagonal close packed metal like magnesium. It is of interest to note that their Debye temperatures vary with temperature equally rapidly although in the opposite direction.

TABLE III

CONSTANT VOLUME HEAT CAPACITIES AND DEBYE CHARACTERISTIC TEMPERATURES OF MAGNESIUM AND CADMIUM

T, °K.	C_v, cal./deg. g. atom Magnesium	Cadmium	Debye characteristic temp., °K. Magnesium	Cadmium
12	0.016	0.392	368	126
16	.042	0.804	357	129
20	.086	1.239	351	134
30	.341	2.300	331	145
50	1.365	3.775	322	159
100	3.724	5.178	323	170
150	4.805	5.557	319	179
200	5.302	5.686	309	194
250	5.557	5.742	297	215
300	5.727	5.785	267	228

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