

TABLE II
LATTICE CONSTANTS OF PURE CALCIUM AND STRONTIUM
HYDROXYAPATITE IN Å.

		This work	Lagergren and Carlström ⁸
CaHA	a_0	9.418 ± 3	9.423
	c_0	6.883	6.884
SrHA	a_0	9.760	9.761
	c_0	7.284	7.277

precipitation from basic solution with subsequent heating to 950°. Under the conditions of these

experiments there is a marked discrimination against strontium in the precipitate. An extension of these data to processes occurring in biological systems of vastly different concentrations and pH is not yet possible. However, nothing has been brought out in this work that would indicate solid solutions of strontium in bone mineral are either unlikely or impossible.

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Magnesium-Cadmium Alloys. X. Heat Capacity of MgCd between 20 and 270° and a Final Evaluation of the Residual Entropy of the MgCd Superlattice¹

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The heat capacity of MgCd has been measured between 25 and 270° by adiabatic calorimetric techniques permitting a precision of 0.1 to 0.2% in the measurements. The data show a sharp first degree transition at about 251° superimposed upon a broad second degree "order-disorder" transition of the type customary for such alloys. With the aid of the heat capacity data, the residual entropy of MgCd has been calculated to be 0.035 ± 0.04 e.u./g. atom. Standard heats, free energies and entropies of formation of the alloy at 270°, which were reported earlier, have been corrected to 25°. Transition energy and temperature agree well with values reported by other investigators.

In paper V of this series heat capacity data for MgCd between 12 and 320°K. were presented.³ The entropy of formation of this substance at 270° had been determined⁴ by the electrochemical cell method and in paper V the two sets of data were used to evaluate the residual entropy of the compound MgCd. The required thermal data above 320°K. for MgCd and for the pure metals were taken from the literature.

In this paper heat capacity data for MgCd from 20 to 270° are presented. These data together with heat capacities of the pure metals⁵ recently determined in the same apparatus and the entropy of formation at 270° of MgCd are used to evaluate the residual entropy of the MgCd superlattice.

Experimental

Apparatus.—Full descriptions of the calorimetric equipment used may be found elsewhere.⁶⁻⁹

Materials Used.—The sample employed was the same as had been used in the earlier work.³ Its composition was

50.52 ± 0.04 atomic % cadmium. The mass of the sample was 429.281 g. (*in vacuo*) or 6.2375 gram atoms of alloy.

Method of Measurement.—The intermittent heating technique has been used in this study. Heat is applied to the sample for a carefully measured interval of time of 5 to 15 minutes resulting in a temperature increment of roughly 5°. Temperature is then measured until it becomes constant, or at least until the drift is very small (10^{-3} deg./min.).

In contrast to the long equilibration times experienced with MgCd₂ and Mg₃Cd, as described in paper VIII⁹ of this series, "normal" equilibration times of 20 to 30 minutes were observed in the measurements on MgCd below and above the "order-disorder" Curie point at 251°.

Transition Experiments.—The transition temperature could not be determined by a single direct measurement. The sample absorbed a large amount of energy from 251.08 to 251.30°. This range was obtained from the results of four partial heatings into the transition in which the heating was stopped periodically and the equilibrium temperature determined.

The energy absorbed by the sample in this 0.22° region was measured in two separate experiments. In each experiment the sample was continuously heated from a temperature below the transition to a temperature above the transition. The energy absorbed from 251.08 to 251.30° could then be calculated from a knowledge of the appropriate heat capacities of the sample below and above the transition.

Results

The data for MgCd were obtained in 15 series of measurements including transition point experiments involving a total of 126 determinations. The experimental details of each series of determinations are too numerous to relate here.¹⁰

Smoothed values for the heat capacities are given in Table I. Excluding the region immediately below the transition, where the heat capacity is rising sharply, the precision of the measurements is 0.1 to 0.2% as judged from the scatter of points from a smooth curve.

(10) These details are given in ref. 7.

(1) This work was supported by a grant from the U. S. Atomic Energy Commission.

(2) From a thesis submitted by K. F. Sterrett in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, June, 1957.

(3) C. B. Satterthwaite, R. S. Craig and W. E. Wallace, *THIS JOURNAL*, **76**, 232 (1954).

(4) F. A. Trumbore, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 132 (1952); **76**, 6417 (1954).

(5) W. G. Saba, K. F. Sterrett, R. S. Craig and W. E. Wallace, *ibid.*, **79**, 3637 (1957).

(6) W. V. Johnston, Ph.D. Thesis, University of Pittsburgh, August 1955.

(7) K. F. Sterrett, Ph.D. Thesis, University of Pittsburgh, June 1957.

(8) W. E. Wallace, R. S. Craig and W. V. Johnston, U. S. Atomic Energy Commission Report, No. NYO-6328, Oct. 1955. This document is available from the U. S. Government Printing Office.

(9) W. V. Johnston, K. F. Sterrett, R. S. Craig and W. E. Wallace, *THIS JOURNAL*, **79**, 3633 (1957).

TABLE I
 HEAT CAPACITY OF MgCd

T, °K.	C _p , cal./deg. g.-atom	T, °K.	C _p , cal./deg. g.-atom
298.16	6.16	470	8.26
300	6.17	475	8.41
310	6.23	480	8.56
320	6.30	485	8.73
330	6.37	490	8.93
340	6.45	495	9.17
350	6.54	500	9.45
360	6.64	505	9.81
370	6.74	510	10.22
380	6.84	515	10.74
390	6.94	520	11.48
400	7.05	524.24	12.83
410	7.19	524.46	...
420	7.33	525	7.66
430	7.47	530	7.49
440	7.63	535	7.45
450	7.80	540	7.43
460	8.01	543.16	7.43

Residual Entropy.—The entropy of formation of MgCd at 270° was reported earlier as 1.09 e.u. based on the electrochemical cell method.⁴ Using the heat capacity data for the pure metals⁵ recently determined with the high temperature calorimeter together with earlier data from this Laboratory for the low temperature region,¹¹ one computes entropies at 270° to be 11.56 e.u. for Mg and 16.28 e.u. for Cd. From these data one calculates the entropy of an alloy of this stoichiometry (50.52 at. % Cd) to be 15.03 e.u. at 270°. The data in the present paper combined with earlier results³ permit the calculation of $S_{543.16} - S_{0^\circ\text{K}}$ for MgCd. This ΔS is found to be 14.96 e.u. from which one computes the residual entropy as 0.07 e.u.

This entropy value so computed represents what may be designated as an uncorrected value. Paper VII⁹ explains in detail how mobility ceases on cooling magnesium-cadmium alloys to low temperatures, causing some high-temperature configurations to be frozen-in and resulting in a small amount of residual entropy. Satterthwaite applied the Bragg-Williams¹² theory to his data and estimated the residual entropy at 0°K. due to this factor as less than 0.01 e.u.¹³

A further source of residual entropy is the lack of stoichiometry of the alloy. Satterthwaite estimated this to be 0.03 e.u. using an expression derived by C. Wagner¹⁴

$$S = -R \left[\Delta X_1 \ln \left(\Delta X_1 \frac{V_1 + V_2}{V_2} \right) - \Delta X_1 \right]$$

where V_1 and V_2 are the atomic fractions of the components for exact stoichiometric ratios (1:1

(11) R. S. Craig, C. A. Krier, L. W. Coffer, E. A. Bates and W. E. Wallace, *THIS JOURNAL*, **76**, 238 (1954).

(12) W. L. Bragg and E. J. Williams, *Proc. Roy. Soc. (London)*, **145A**, 699 (1934).

(13) C. B. Satterthwaite, Ph.D. Thesis, University of Pittsburgh, June, 1950.

(14) G. Massiug, "Handbuch der Metallphysik," Band I, Zweiter Teil, Chapter III, pp. 48-52.

in this case) and ΔX_1 is the excess of one component defined as $\Delta X_1 = X_1 - V_1/(V_1 + V_2)$.

After assuming that 0.005 e.u. is a good estimate of the "frozen-in" disorder, correcting for non-stoichiometry and using the best estimates of error of the various quantities entering the calculation, one obtains 0.035 ± 0.04 e.u. as a corrected value for the residual entropy of MgCd. Thus, within the limit of experimental error, MgCd is found to obey the Third Law of Thermodynamics.

Transition Temperature of MgCd.—The data obtained from the four partial heating experiments are shown in Table II. The transition region can be determined from a plot of these measurements as extending from 251.08 to 251.30°.

 TABLE II
 TRANSITION EXPERIMENTS

Fraction transformed	Temp., °C.
0.04	251.10
.08	251.15
.21	251.21
.76	251.30

Transition Energy of MgCd.—The two transition energy determinations yielded 357.03 and 356.96 cal./g.-atom as the energy absorbed from 251.08 to 251.30°. These results yield an average value of 357.0 cal./g. - atom. Error due to the extrapolations is estimated to cause an uncertainty of ± 1 cal./g.-atom in this value.

Standard Heats, Free Energies and Entropies of Formation at 25°.—Using the present heat capacity data it is possible to correct the values reported earlier at 270 to 25°. Results of these calculations are shown in Table III.

 TABLE III
 STANDARD HEATS, FREE ENERGIES AND ENTROPIES OF FORMATION OF MgCd AT 25°

ΔH_f (cal./g.-atom)	-1920 ± 11
ΔF_f (cal./g. atom)	-1857 ± 21
ΔS_f (e.u./g.-atom)	-0.21 ± 0.03

The uncertainties are rough estimates based upon the uncertainties in the experimental quantities involved in the calculations.

Buck, Wallace and Rulon¹⁵ measured ΔH_f for this alloy at 25° in a differential solution calorimeter. They obtained -1960 ± 50 cal./g.-atom. The excellent agreement between this value and the present data in contrast to the poorer agreement reported for Mg₃Cd in Paper VIII⁹ supports the explanation⁹ that the difference in ΔH_f for Mg₃Cd may have been due to disorder frozen into their samples at a higher temperature. In this research it was observed that it was not possible to freeze disorder into MgCd by quenching the sample from above the Curie point to room temperature. In all probability Buck's measurements on MgCd were on a homogeneous ordered sample.

(15) T. M. Buck, Jr., W. E. Wallace and R. M. Rulon, *THIS JOURNAL*, **74**, 136 (1954).

Discussion of Results

Heat Capacities.—Hirabayashi, *et al.*¹⁶⁻¹⁸ and Khomyakov, *et al.*,¹⁹ have measured the heat capacity of various alloys with compositions fairly near to MgCd. Both investigators employed adiabatic calorimetry, but they used the continuous heating technique. Their results agree with the present data in regard to the first degree nature of the transition at about 251° which is superimposed upon the broad second degree "order-disorder" transition. Table IV shows that the exact transition temperature and transition energy depend upon the composition. Composition differences make a detailed quantitative comparison of heat capacities seem unwarranted.

An integration of the data reported by Khomyakov, *et al.*, from 298.16 to 543.16°K. for the 1:1 alloy results in an entropy value of 5.08 e.u., which is slightly lower than the 5.13 e.u. obtained in the present investigation. This difference might be attributed to the continuous heating technique which, when applied to systems exhibiting order-disorder transformations, tends to displace energy to higher temperatures and thus lower the observed entropy.

(16) M. Hirabayashi, S. Nagasaki, H. Maniwa and H. Nagasa, *J. Jap. Inst. Met.*, **13**, 1 (1949); **13**, 6 (1949).

(17) M. Hirabayashi, H. Maniwa and S. Nagasaki, *ibid.*, **14B**, 6 (1950).

(18) M. Hirabayashi, *ibid.*, **16**, 285 (1952).

(19) K. G. Khomyakov, V. A. Knoller and V. A. Troshkina, *Vestnik Moskov Univ.*, Vol. V, No. 6, Ser Fiz-Math i Estest Nauk, No. 4, p. 43 (1950).

TABLE IV

COMPARISON OF ΔH OF TRANSITION AND TRANSITION TEMPERATURES FOR VARIOUS COMPOSITIONS

Compn., at % Cd	Present data		Hirabayashi		Khomyakov	
	ΔH_{Trans}	T_{Trans}	ΔH_{Trans}	T_{Trans}	ΔH_{Trans}	T_{Trans}
51.0				360		
50.8				250°		
50.52 ± 0.04	357.0	251.30°				
50.00				251.84°	362	251.5°
49.5				400		
49.44					362	250.2°

The present data join smoothly below 280°K. to that reported earlier³ for the low temperature region. Above 280°K. the earlier data are slightly higher, reaching a maximum deviation of 0.24% at 300°K. The earlier data were taken with the original version of the low temperature calorimeter developed in this Laboratory. Heat capacities of cadmium measured in the same calorimeter were also shown to be high in the upper range of the instrument. The discrepancy was explained by Craig, *et al.*,¹¹ as resulting from faulty design of the earlier calorimeter which permitted some heat to be lost from the sample *via* the lead wires. All other heat capacity measurements on Mg-Cd alloys in this Laboratory have been made with an improved version of the calorimeter in which this fault has been corrected.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY AND UNIVERSITY OF NORTH CAROLINA]

Correlation of Turbidity and Activity Data for Aqueous Solutions of the Tungstophosphoric Acids¹

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Good agreement was obtained between the turbidities of 9- and 12-tungstophosphoric acid from light scattering and those calculated from activity data. The activity data were obtained from isopiestic vapor pressure measurements. Turbidities calculated on the basis of ideal behavior are considerably different.

Introduction

In an earlier light scattering study² of 9- and 12-tungstophosphoric acids, the usual Debye Hc/τ versus c extrapolation³ led to molecular weights in agreement with the dimeric formulation of the 9-acid ($H_6P_2W_{18}O_{62}$), and the monomeric formulation of the 12-acid, ($H_7PW_{12}O_{42}$), when organic solvents were used.

However, in aqueous solution,^{2,4} the apparent molecular weights obtained were only a fraction of the empirical formula weights. This difference may be attributed to the dissociation of these acids to highly charged ions in aqueous solution,^{5,6}

leading to deviations from ideality. Accordingly, the approximations used in the Debye treatment are no longer applicable.

In order to interpret the turbidity of such systems it is necessary to use activity data. We have determined the vapor pressure over these solutions by the isopiestic method from which the activity of water was obtained. When these results were used in the appropriate expression for the turbidity, the calculated and experimental turbidities were in good agreement.

Experimental

The tungstophosphoric acids were prepared and purified as described earlier.⁴ The density data were obtained at 25° with a Gay-Lussac type specific gravity bottle. Earlier data obtained by Soboleff⁷ could not be utilized.

The isopiestic vapor pressure data were obtained using equipment and technique previously described.⁸

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(3) P. Debye, *J. Phys. Chem.*, **51**, 181 (1947).

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