

[CONTRIBUTION NO. 891 FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF PITTSBURGH]

Magnesium-Cadmium Alloys. VII. Low Temperature Heat Capacities of MgCd_3 and Mg_3Cd and a Test of the Third Law of Thermodynamics for the MgCd_3 Superlattice^{1,2}

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RECEIVED APRIL 4, 1953

Heat capacities between 12 and 320°K. are presented for alloys containing 24.98 and 74.98 atomic per cent. cadmium. These data are used to calculate entropies at 25° relative to absolute zero. From these results and additional data in the literature the residual entropy of MgCd_3 has been computed to be 0.21 e.u./g. atom. This has been accounted for in terms of frozen-in Schottky defects, which at 25° are present to 1.7%. The measured heat capacities deviate appreciably from the values expected from the Kopp-Neumann rule. The experiments have revealed a broad solid state transition in Mg_3Cd beginning at about the ice point and one or possibly two such transitions in MgCd_3 between 182 and 320°K.

In paper V of this series³ (hereinafter referred to as V) low temperature heat capacities of the MgCd superlattice were presented and the data were used to determine the residual entropy of MgCd . This paper presents similar data for MgCd_3 and Mg_3Cd , except that for the latter alloy the high temperature heat capacities are so discordant that a reliable residual entropy calculation is not possible.

Experimental

Calorimetric Apparatus.—This was identical with that used in V except that the sample container was the modified version described⁴ in paper VI of this series.

Preparation, Analysis and Heat Treatment of Samples.—Except for the details of the heat treatment the procedure was identical with that used in V. The results of the analyses were 74.98 ± 0.04 and 24.98 ± 0.04 atomic per cent. cadmium.

To ensure homogeneity the alloys were kept molten for about 0.5 hr. and were stirred 100 times with a reciprocating stirrer. The cast ingots were then heat treated for further homogenization as follows: MgCd_3 at 290 to 300° for 30 days, Mg_3Cd at 345 to 350° for 47 days. They were then machined to a size and shape suitable for the calorimeter and returned to the annealing oven for an additional two-day period to remove strains. MgCd_3 was given further heat treatments as follows: it was removed from the 350° oven and placed in an oven at 295° for 11 days and then held at 130°, 25° below the order-disorder transition point, for 18 days to develop the MgCd_3 superlattice. The adequacy of this time was established from Stepanov and Kornilov's studies⁵ of the kinetics of the ordering process in Mg_3Cd and were confirmed by observations in this study which are referred to below. Since Stepanov and Kornilov found⁶ rapid ordering in quenched MgCd_3 at the ice point, no low temperature heat treatment of this alloy was necessary.

The quantities used in the heat capacity measurements were 597.991 g. or 6.6171 g. atoms of MgCd_3 and 262.179 g. or 5.6596 g. atoms of Mg_3Cd . Atomic weights used were Mg, 24.32 and Cd, 112.41.

Experimental Results

The Low Temperature Transitions.—In V it was shown that the effect of the change in order became apparent in the heat capacity measurements of MgCd at about 230°K., fully 300° below the order-disorder transition point. Thus with

MgCd_3 and Mg_3Cd , whose transition points lie at temperatures considerably lower than for MgCd , it was anticipated that the measurements would be affected by configurational changes at possibly even lower temperatures. Hence, considerable care was necessary to be assured that reasonably reliable data were obtained in the temperature range immediately below the ice point. This aspect of the work can better be presented after a brief discussion of the phenomena which are ascribed to the low temperature transitions.

In V it was indicated that at temperatures between 230 and 260°K. temperature equalization in MgCd was abnormally slow after the addition of heat. On raising the temperature of the sample a downward drift in temperature set in which persisted for hours, and a cooling of the specimen was followed by an upward drift in sample temperature for hours. These temperature drifts were attributed to changes in degree of order with time. Initially, the system has a certain temperature and a configuration characteristic of that temperature. When the temperature is changed, there is a new equilibrium configuration and the system relaxes toward the new configuration with an adsorption or evolution of heat, depending on whether its initial degree of order is too low or too high.

Heat capacity measurements on Mg_3Cd and MgCd_3 revealed slow temperature equalization at low temperatures similar to that observed with MgCd and described in V. First, consider MgCd_3 . A sample was carefully cooled (as described in the next section) to liquid air temperatures and a series of measurements was begun in which the temperature was raised toward room temperature in stepwise fashion. Up to 177°K. the behavior was normal in that the temperature became constant about 0.5 hr. after the energy input was stopped. In the next determination the sample temperature was raised to 182°K. and there was noticed a tiny upward drift of 3×10^{-5} deg./min. which persisted for hours. Apparently up to approximately 180°K. the state of the system was frozen-in. The upward drifts, which at first were barely perceptible, became with increasing temperature more pronounced for about 20° and then diminished until at 208°K. a downward drift set in. Above 208°K. the downward drifts became stronger and above 225°K. the time required for attaining a constant temperature became shorter until at

(1) From a thesis submitted by L. W. Coffey in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, January, 1953.

(2) This work was assisted by the Atomic Energy Commission.

(3) C. B. Satterthwaite, R. S. Craig and W. E. Wallace, *THIS JOURNAL*, **75**, 232 (1953). This paper gives references to earlier papers in the series.

(4) R. S. Craig, C. A. Krier, L. W. Coffey, E. A. Bates and W. E. Wallace, *ibid.*, **75**, 238 (1953).

(5) N. I. Stepanov and I. I. Kornilov, *Ann. Secteur anal. phys.-chim., Inst. Chim. gen. (U.S.S.R.)*, **10**, 78 (1938).

(6) N. I. Stepanov and I. I. Kornilov, *ibid.*, **10**, 97 (1938).

240°K. the behavior was again normal, *i.e.*, temperature equilibration within about 0.5 hr. These observations indicated that a sample cooled according to the program given in the next section exists at temperatures below 180°K. in the frozen-in state characteristic of about 208°K. and that above 180°K. the sample relaxes toward an equilibrium state with a rate which increases with temperature up to 240°K., at which point the process becomes so rapid that it is lost against the background of the normal heat distribution characteristics of the system.

On this basis it was anticipated that at still higher temperatures the time of relaxation would be further shortened and no drifts would be observed. This was not the case. Beginning again at 283°K. downward drifts were observed and these continued up to 324°K., the highest temperature that could be studied with the present equipment. At 324°K., the initial drift rate after raising its temperature from 319°K. was -7.31×10^{-3} deg./min. and 8 hr. later it was still falling at the rate of 1.7×10^{-4} deg./min.

At present, the nature of the processes responsible for the thermal behavior just described is not known. In fact, one cannot be sure that there are two processes. There is some indication that the temperature coefficient of the process occurring above 283°K. is negative⁷ and so it is possible that there is a single process which has a rate which increases with temperature between 182 and 240°K., reverses itself somewhere between 240 and 283°K. and then becomes slow enough to be observable again at 283°K. and above.⁸ Considering the possibility that there are two processes, it has been shown⁹ that the axial ratio in MgCd₃ is a strong function of the degree of order. Thus, when the order parameter changes, crystallographic alterations ensue, at least above 25°. In polycrystalline materials such crystallographic changes should have a considerable energy of activation and would become frozen-in at a relatively high temperature. Following the conclusions reached in V concerning MgCd one might attribute the process beginning at 182°K. to the change of the degree of order of the system, the axial ratio being frozen-in at this low temperature. Such a process can occur by a motion of vacancies over a lattice of fixed geometry and should have a relatively low energy of activation. At higher temperatures the axial ratio "becomes unfrozen" and varies with order (and temperature). It is possible that the process occurring at 283°K. and above is the relaxation of the axial ratio toward different equilibrium values as the temperature is changed. Some support is provided for this point of view by noting that in MgCd the variation of the degree of order with temperature is quite rapid at 25° while the crystallographic change (orthorhombic to hexagonal) accompanying the order-disorder transi-

tion exhibits¹⁰ very pronounced hysteresis effects at temperatures roughly 200° higher.

No drifts which could be attributed to the sample were observed below 260°K. in the determinations of the heat capacities of Mg₃Cd. Slight upward drifts were noticed between 268 and 306°K. at which point the drift became reversed. Above the reversal points the drifts were the largest so far observed with any of the magnesium-cadmium alloys. Several experiments were performed to establish the factors controlling the reversal temperature T_r . For a sample which had been held for some hours at 325°K., quenched to liquid air temperatures and then rapidly warmed up to prevent alterations in the quenched material T_r was 317°K. In the region around T_r , samples in non-equilibrium states had apparent specific heats differing by as much as 10% from the equilibrium state values. The large differences were caused by the heat effects which accompanied the approach of the sample to equilibrium, producing significant alterations in sample temperature during an experiment. These several observations clearly indicated that some process is initiated in Mg₃Cd by an alteration in temperature and it seems probable that it is the variation of the degree of order.

Heat Capacities.—The experiments were performed and the data treated so as to obtain results corresponding as closely as possible to the equilibrium state of the alloys. The samples were cooled very slowly through the temperature range where the above-mentioned slow processes were occurring. With MgCd₃ the temperature was reduced to the Dry Ice point at the rate of 6°/hr. and the system was then allowed to stand overnight at this temperature before making measurements upward or cooling further for lower temperature experiments. With this technique, measurements

TABLE I
ATOMIC HEAT CAPACITIES OF MgCd₃ AND Mg₃Cd

Temp., °K.	C _p , ^a cal./deg. atom Mg ₃ Cd	C _p , ^a cal./deg. atom MgCd ₃	Temp., °K.	C _p , ^a cal./deg. atom Mg ₃ Cd	C _p , ^a cal./deg. atom MgCd ₃
12	0.052	0.183	150	5.031	5.541
14	.096	.286	160	5.154	5.617
16	.159	.448	170	5.262	5.681
18	.233	.619	180	5.358	5.728
20	.306	.788	190	5.441	5.774
25	.520	1.283	200	5.517	5.854
30	.769	1.785	210	5.587	5.951
35	1.048	2.183	220	5.649	6.060
40	1.340	2.557	230	5.705	6.171
45	1.631	2.909	240	5.755	6.275
50	1.922	3.210	250	5.803	6.377
60	2.495	3.722	260	5.847	6.481
70	2.960	4.117	270	5.885	6.590
80	3.383	4.442	280	5.909	6.732
90	3.753	4.714	290	5.921	6.920
100	4.041	4.913	298.16	5.938	7.079
110	4.303	5.085	300	5.940	7.118
120	4.523	5.222	310	6.408	7.404
130	4.717	5.353	320	7.258	8.009
140	4.888	5.140			

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

(7) R. S. Craig, unpublished calculations.

(8) Such reversals are frequently observed in solid state reactions. For example, this has been observed by J. Nyström (*Archiv. Fysik*, **2**, 151 (1950)) for the ordering of AuCu and E. Scheil and H. Stadelmaier (*Z. Metallkunde*, **43**, 227 (1952)) for precipitation in NaCl-KCl solutions.

(9) E. A. Edwards, W. E. Wallace and R. S. Craig, *This Journal*, **74**, 5256 (1952).

(10) Unpublished measurements of D. A. Edwards, J. D. Phillips and W. E. Wallace.

below 182°K. were free from drifts. Between 182 and 208°K. the drifts were small and introduced negligible error into the heat capacities. The slowness in reaching equilibrium between 208 and 240°K. was more important and so this range was covered several times with varying procedures. The accepted results were obtained in two measurements extending from 208 to 225°K. and from 225 to 240°K., the temperature being followed for approximately 8 hr. after the first of the heatings, until it steadied off. When drifts were found with either alloy, the rating periods were lengthened until the drifts disappeared or became constant and small and a suitable correction was made. Smoothed data are presented in Table I.

Entropy Change between 0°K. and 25°C.—The gain in entropy above 12°K. was evaluated by graphical integration of the results in Table I. The T^2 law was assumed to hold below 12°K. The calculations are summarized in Table II.

TABLE II
ENTROPY CHANGE BETWEEN 0°K. AND 25°C.

Temp. region, °K.	ΔS , e.u./g. atom	
	MgCd ₃	Mg ₃ Cd
12–298.16	11.15	8.69
0–12 (extrap.)	0.06	0.02
0–298.16	11.21	8.71

Precision of Experimental Quantities.—The average percentage deviation of the individual determinations from a smooth curve was obtained as in V. With MgCd₃, the percentage error in C_p was 2.8, 0.03, 0.02 and 0.06 in the temperature ranges 12–30, 30–70, 70–195 and 195–320°K., respectively. The corresponding quantities for Mg₃Cd were 2.1, 0.2, 0.02 and 0.06. These random errors in C_p produce no more than 0.1% error in the ΔS values for heating from absolute zero to 25°.

Derived Results

Deviations from the Kopp–Neumann Rule.—In V it was pointed out that the Kopp–Neumann rule (additivity of heat capacities) is tacitly assumed to be valid in statistical treatments¹¹ of solid solutions in which they are regarded as regular assemblies.¹² The rule has been widely used in metal physics, because there are few experimental data for alloys, notwithstanding the fact that it has neither an experimental nor a theoretical basis. The heat capacity data in this paper constitute further

TABLE III
 ΔC_p VALUES FOR MAGNESIUM-CADMIUM ALLOYS

T, °K.	ΔC_p , cal./deg. g. atom		
	MgCd ₃	MgCd	Mg ₃ Cd
20	–0.164	–0.133	–0.068
40	–.012	–.043	–.051
60	+ .021	–.081	–.041
80	.007	–.100	–.082
100	.012	–.088	–.094
150	.011	–.056	–.063
200	.032	–.022	–.037
250	.375	.005	–.011
300	.962	.101	–.069

(11) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, 1939, p. 568.

(12) Reference 11, p. 245.

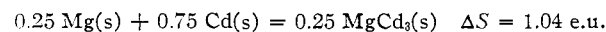
evidence that appreciable deviations from the Kopp–Neumann rule occur. The differences in C_p between an alloy and the equivalent mixture are listed in Table III along with data for MgCd from V.

There appear to be some systematic trends in the ΔC_p data. Each superlattice at 20°K. has a heat capacity about 20% lower than the mixture. These negative deviations tend to disappear with increasing temperature but less rapidly the greater their magnesium content. In fact with Mg₃Cd, ΔC_p is still negative at 300°K. where the configurational contribution is appreciable. These trends have a fairly simple qualitative explanation.

Various lines of evidence point to the fact that the cadmium lattice is greatly disturbed by the incorporation of magnesium, much more so than for the converse process, *i.e.*, introducing cadmium into the magnesium lattice. The flatness of the solidus,¹³ the positive volume change,¹⁴ the anomalously large entropy,¹⁵ the exceptional number of lattice imperfections¹⁶ and the low temperatures required to develop the superlattices in the cadmium-rich alloys all indicate considerable weakening of the cadmium lattice by magnesium compared to the behavior expected from the exothermal nature of the process.¹⁵ This is also borne out by the high heat capacities of MgCd₃ (positive deviations from the Kopp–Neumann rule) between 150 and 200°K. where configurational effects are absent. MgCd and Mg₃Cd conform more nearly to the behavior expected of exothermally formed alloys in that their ΔC_p 's are predominantly negative. The positive ΔC_p 's above 200°K. are largely, if not entirely, due to the configurational contribution, which becomes increasingly more important above 200°K. The structure-weakening factors responsible for the positive ΔC_p 's in MgCd₃ between 60 and 200°K. and the tendency in that direction in MgCd between 80 and 150°K. should become less important as the temperature is reduced and the total vibrational energy of the system is diminished. At sufficiently low temperatures one would anticipate negative ΔC_p 's for any exothermally formed alloy and this is indeed what is observed for the three alloys in Table III.

Test of the Third Law of Thermodynamics for the Superlattice (or Intermetallic Compound) MgCd₃

The entropy of formation of MgCd₃ at 270° was determined¹⁵ recently in this Laboratory using the electrochemical cell



From known specific heats of the pure metals^{4,17}

$$0.25 \text{ Mg}(0^\circ\text{K.}) = 0.25 \text{ Mg}(270^\circ) \quad \Delta S = 2.89 \text{ e.u.}$$

$$0.75 \text{ Cd}(0^\circ\text{K.}) = 0.75 \text{ Cd}(270^\circ) \quad \Delta S = 12.19 \text{ e.u.}$$

(13) W. Hume-Rothery and G. V. Raynor, *Proc. Roy. Soc. (London)*, **A174**, 471 (1940).

(14) J. M. Singer and W. E. Wallace, *J. Phys. Colloid Chem.*, **52**, 999 (1948).

(15) F. A. Trumbore, W. E. Wallace and R. S. Craig, *THIS JOURNAL*, **74**, 132 (1952).

(16) D. A. Edwards, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 5256 (1952).

(17) O. Kubaschewski and E. L. Evans, "Metallurgical Thermodynamics," Academic Press, Inc., New York, N. Y., p. 218.

Using these data the absolute entropy of MgCd_3 at 270° is found to be 16.12 e.u./g. atom. The present measurements together with published C_p data¹⁸ for temperatures above 320°K . permit the calculation of $S_{270^\circ} - S_{0^\circ\text{K}}$ for MgCd_3 . The above room temperature data extend to only 430°K . and must be extrapolated for about 110° . Ordinarily such an extrapolation would be rather questionable. In this case C_p is almost constant for the upper 70° on the measured curve so the extrapolation is probably fairly reliable. $S_{270^\circ} - S_{0^\circ\text{K}} = 15.91$ e.u./g. atom, of which approximately 1.2 e.u./g. atom is from the extrapolation above 430°K . Comparing the entropy gain between 0°K . and 270° with the absolute entropy at 270° , one sees that $S_{0^\circ\text{K}} = 0.21$ e.u./g. atom. Similar calculations for Mg_3Cd were made, but existing heat capacity data above 50° are so divergent that no significance could be attached to the results obtained.

(18) K. G. Khomyakov, V. A. Kholler and V. A. Troshkina, *Vestnik Moskov Univ.*, No. 6, Ser. Fiz-Math. i Estest. Nauk No. 4, 5, 43 (1950).

The residual entropy in MgCd_3 can be accounted for if the number of Schottky defects observed¹⁶ at 25° continue to exist at the absolute zero and are randomly distributed over the lattice sites. The number of Schottky defects at 25° is 1.7%. The entropy associated with these defects when randomly distributed is simply the ideal entropy of mixing. This calculates to be 0.17 e.u./g. atom. Experimentally, $S_{0^\circ\text{K}} = 0.21$ e.u./g. atom with a probable error of 0.07 e.u./g. atom, neglecting error in ΔS for the extrapolated region between 430° and 543°K . Thus, the observed residual entropies agree within the limit of error with the value calculated as mentioned. This agreement, while interesting, must be viewed with caution until direct experimental verification is forthcoming that: (1) the number of Schottky defects observed at 25° remain at reduced temperatures and (2) the composition of the superlattice is exactly 75 atomic per cent. cadmium, an assumption involved in arriving at the number of lattice imperfections.

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Concentrated Sulfuric Acid-Water

BY N. C. DENO AND R. W. TAFT, JR.

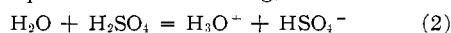
RECEIVED MAY 18, 1953

The H_0 function of Hammett can be precisely evaluated from 83–99.8% (wt.) sulfuric acid and the activity of water can be estimated to a reasonable agreement with experiment from 83 to at least 95% acid. The method assumes that the reaction $\text{H}_2\text{O} + \text{H}_2\text{SO}_4 = \text{H}_3\text{O}^+ + \text{HSO}_4^-$ is of primary importance in determining the properties of these solutions and a mole fraction equilibrium constant of 50 is shown to be applicable for this reaction over the entire range 83 to 99.8% sulfuric acid. These results are interpreted on the basis that the activity coefficients involved approach constancy in 83–99.8% sulfuric acid solutions. This ideal behavior is attributed to the high dielectric constant and similarity of the medium to that of fused salts. Several applications to reaction rates studied in the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system are made. The rate data support the validity of the conclusions reached.

Calculation of H_0 .—Brand¹ has shown that the Hammett acidity function,² H_0 , in the region 90–99.8% sulfuric acid can be calculated by eq. 1

$$H_0 \text{ (calcd.)} = -8.36 + \log X_{\text{HSO}_4^-}/X_{\text{H}_2\text{SO}_4} \quad (1)$$

The ratio of the mole fractions $X_{\text{HSO}_4^-}/X_{\text{H}_2\text{SO}_4}$ are obtained from the stoichiometric amounts of water and sulfuric acid assuming that reaction 2 is complete. This assumption is in close agreement with the Raman spectra work of Young,³ who found that



in this region, the addition of each mole of water gave one mole of bisulfate ion.

Since equimolar water-sulfuric acid corresponds to 84.5% acid, it seemed surprising to us that eq. 1 would fail from 85–90% acid unless reaction 2 was substantially incomplete.

We have found that the calculation of the H_0 function by eq. 1 can be extended with excellent precision to the region 89–83% sulfuric acid if a mole fraction equilibrium constant, K_2 , of 50 is assumed to be valid for reaction 2 over this region.

(1) J. C. D. Brand, *J. Chem. Soc.*, 1002 (1950).

(2) L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

(3) T. F. Young, *Rec. Chem. Progress*, spring issue (1951).

In Table I the observed values of H_0 are compared with values calculated from eq. 1 assuming reaction 2 to be complete (Brand's method¹) and values calculated from eq. 1 using $K_2 = 50$.

On the basis that observed H_0 values are accurate to 0.05 unit, the value 50 for K_2 is precise to ± 10 , since the H_0 values calculated by eq. 1 do not fit experimental values within this limit when larger or smaller values of K_2 are used to calculate the $X_{\text{H}_2\text{SO}_4}/X_{\text{HSO}_4^-}$ ratio. For example, a value of $K_2 = 40$ leads to a deviation of 0.08 between calculated and observed H_0 values for 84.5% acid, the acid concentration for which calculated values are most sensitive to the value of K_2 used.

The following alternate equation can be used for the computation of H_0

$$H_0 = -6.66 + \log X_{\text{H}_2\text{O}}/X_{\text{H}_3\text{O}^+} \quad (3)$$

Equations 1 and 3 are equivalent by virtue of the mole fraction equilibrium constant for reaction 2 which can be written in the form

$$\log \frac{X_{\text{HSO}_4^-}}{X_{\text{H}_2\text{SO}_4}} - \log \frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_3\text{O}^+}} = \log K_2 = 1.70 \quad (4)$$

In a later section $\log f_{\text{H}_2\text{O}}$ is evaluated, where f is the activity coefficient. Reference to Table III