internal equilibrium. Gillespie and Perry[16] have in fact observed several abnormal 0° isotherms for which no break at all occurs.

The second isotherm break occurs at Pd_2H from 80 to 200°. The break occurs at higher hydrogen concentrations at lower temperatures possibly because of hydrogen adsorption in structural rifts and defects caused by the independent expansion of each lattice cube.

Significance of the Entropy of Pd_2H at 0°K.—In the preceding paper[2] a residual entropy of 0.59 e.u. at 0°K. was compared to the residual entropy of 0.82 e.u. for ice on the basis that random hydrogen bonding can occur in both. In ice, each oxygen atom is surrounded by four tetrahedrally arranged hydrogen atoms. In $PdH_4 \cdot 7Pd$, only some of the palladium atoms are surrounded by four tetrahedrally arranged hydrogen atoms. For ice, however, only two hydrogen atoms are covalently bound at one time to an oxygen atom while all four hydrogen atoms can be covalently bound to the central palladium atom. Just as random distribution of hydrogen atoms in ice is frozen into a false equilibrium at low temperatures, the arrangement in Pd_2H is subject to a similar circumstance. In building a model of $PdH_4 \cdot 7Pd$, many different arrangements of the PdH_4 molecules on corner lattice sites can be constructed. Actually there are five possible arrangements for the distribution in an independent lattice cube, but the cubes are not independent in the metal. The arrangement of PdH_4 molecules in one cube partially determines the arrangement in the neighboring cubes. The system is too complex to lend itself to a numerical calculation of the total number of arrangements as can be done in the case of ice. However, since each cube is equivalent to two Pd_2H molecules, the experimental value of 0.59 e.u. allows the choice of two arrangements for the PdH_4 molecules in each cubic lattice because

$$S_0 = k \ln 2^{N/2} = {}^1/_2 R \ln 2 = 0.69 \text{ e.u.} \qquad (2)$$

Comparison with Free Proton Theory.—It must be remembered that the degree of hydrogen bonding in palladium hydride is changing with temperature as indicated by the heat capacity curve. It is apparent that the covalently bonded hydrogen model at high temperatures becomes a model of interstitial hydrogen atoms vibrating and rotating relative to the palladium lattice. This assembly of hydrogen atoms, even though the hydrogen atoms share electrons with individual palladium atoms, would be indistinguishable from the model of free protons assembled in regular monolayers as considered by Lacher.[17] The straight line relation in the α-phase between hydrogen concentration and the square root of hydrogen pressure applies equally to a PdH covalently bound hydrogen model or to a free proton model. In other words, much that has been explained in the past on the basis of free protons can also be explained by the covalently bound hydrogen. Additional investigations, particularly of neutron diffractions, will have to be conducted at temperatures well below room temperature in order that the covalently bound hydrogen model be further verified.

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[16] L. J. Gillespie and J. H. Perry, *J. Phys. Chem.*, **35**, 3367 (1931).

[17] J. R. Lacher, *Proc. Roy. Soc.* (*London*), **161**, 525 (1937).

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[CONTRIBUTION NO. 1008 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Magnesium–Cadmium Alloys. VIII. Heat Capacities of Mg_3Cd and $MgCd_3$ between 20 and 290°. The Standard Heats, Free Energies and Entropies of Formation and the Residual Entropies[1,2]

BY W. V. JOHNSTON, K. F. STERRETT, R. S. CRAIG AND W. E. WALLACE

RECEIVED MARCH 23, 1957

Heat capacities of $MgCd_3$ and Mg_3Cd have been measured between 25 and 270° using a new adiabatic calorimeter permitting a precision of 0.1 to 0.2% in the measurements. Experiments were performed using an intermittent heating technique in order that equilibrium heat capacities might be obtained. The data reveal a specific heat anomaly of the customary type for alloys undergoing order–disorder transitions, with peak values at 83.8 and 150.6° for $MgCd_3$ and Mg_3Cd, respectively. With the aid of the heat capacity data, the standard heats, free energies and entropies of formation of the alloys at 270°, which were reported earlier, have been corrected to 25°. The residual entropy of Mg_3Cd has been found to be 0.03 ± 0.04 e.u./g. atom and the corresponding quantity for $MgCd_3$ has been found to be 0.16 ± 0.04. The latter is in good agreement with the quantity 0.17 ± 0.01 e.u. computed statistically under the assumption that there is a random distribution of the observed number of Schottky defects over the lattice sites. Attention is directed to the large errors which can occur when the conventional continuous heating technique is used with systems undergoing configurational changes.

In Paper VII of this series heat capacity data for Mg_3Cd and $MgCd_3$ between 12 and 320°K. were presented.[3] Entropies of formation of these two substances at 270° had been determined[4] earlier by the electrochemical cell method and in

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

[2] From a thesis submitted by W. V. Johnston in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, August, 1955.

[3] L. W. Coffer, R. S. Craig, C. A. Krier and W. E. Wallace, THIS JOURNAL, **76**, 241 (1954).

[4] F. A. Trumbore, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 132 (1952).

paper VII the two sets of data were used to evaluate the residual entropy of the compound $MgCd_3$. The required thermal data above 320°K. were taken from the literature. A similar calculation for Mg_3Cd was not possible at that time because of the unreliability of the heat capacity data for it above 320°K. In fact the calculation for $MgCd_3$ was not entirely satisfactory since the existing data extended only to 430°K. and an extrapolation over an interval of 110° had to be made. To permit a satisfactory evaluation of the residual entropies of these substances a new calorimeter has been built and used to determine their heat capacities between 20 and 290°. The data obtained are of additional interest in that (1) they permit reliable evaluations of the heats, free energies and entropies of formation of the two compounds at 25° and (2) they indicate for the first time the temperature dependence of the *equilibrium* heat capacities in the region where these substances exhibit thermal anomalies due to order–disorder transformations. Previous studies have consistently involved the continuous heating technique yielding *non-equilibrium* heat capacities, which for these materials differ at some temperatures appreciably from the equilibrium values.

Experimental

Apparatus.—Since full descriptions of the calorimetric equipment used may be found elsewhere,[5,6] only a brief account will be given here. The calorimeter assembly was essentially of the Southard–Brickwedde design.[7] A few departures from conventional practice were necessary because of the higher temperatures involved. Wires were insulated with glass braid (instead of Nylon) impregnated with either Teflon or a silicone resin. The sample container was very similar to that which has been used[3] in this Laboratory for several years in the study of intermetallic compounds at low temperatures. It was sealed off using a solder consisting of Pb with 5% Ag added. This proved to be more satisfactory mechanically than pure Pb which was originally used. The sample was sealed off in an enclosed container which permitted the soldering to be done under reduced pressure. About 0.1 atm. pressure of helium exchange gas was introduced. Temperatures were measured with a capsule type platinum resistance thermometer that had been calibrated by the National Bureau of Standards. Its fundamental interval was periodically redetermined during the course of the work.

Materials Used.—The samples employed were the same as had been used in the earlier work.[3] They had been stored under an atmosphere of helium while not in use. Compositions were 74.98 ± 0.04 and 24.98 ± 0.04 atomic % cadmium for $MgCd_3$ and Mg_3Cd, respectively. The masses of sample employed were: $MgCd_3$, 582.207 g. or 6.4425 g. atoms; Mg_3Cd, 252.092 g. or 5.4418 g. atoms.

Method of Measurement.—$MgCd_3$ and Mg_3Cd undergo order–disorder transitions in the temperature range covered at about 85 and 150°, respectively. Most of the heat capacity data for alloys in the order–disorder region have been obtained using the continuous heating technique. It appears that such results may in certain regions of temperature be seriously in error (10% or more) due to the failure to maintain equilibrium in the sample. Disordering requires a redistribution of atoms over the positions in the lattice and this may fail to keep pace with the changing temperature when continuous heating is used. In this event the measured heat capacity is a non-equilibrium value and is therefore not suitable for entropy calculations.

The intermittent heating technique has been employed in the present study. The sample is heated for a carefully measured interval of time of 5 to 15 minutes duration resulting in a temperature increment of roughly 5°. Temperature was then followed until it became constant,[8] if this occurred in a reasonable length of time. This was not feasible with Mg_3Cd from 35 to 60° and with $MgCd_3$ from 31 to 95°. In these ranges the temperature continued to fall for many hours after the heat input was stopped, indicating that disorder in the sample was continuing to increase. In some instances the course of the temperature–time curve was followed for 20 hr. and the sample had not reached configurational equilibrium. In these cases an extrapolated final temperature was found under the assumption that the temperature tends exponentially toward the equilibrium value, an assumption which has been justified by recent kinetic studies[9] of the order–disorder transformation in $MgCd_3$.

With Mg_3Cd the extrapolations were short and errors introduced from this source were slight. The extrapolations were not short, however, for temperatures near the order–disorder Curie point for $MgCd_3$. Equilibration was so sluggish that errors of several *per cent.* were possible at temperatures between 70 and 80°. Accordingly three determinations were made of the total change in enthalpy for $MgCd_3$ on heating it from 50 to 100°. It was carefully maintained at the lower temperature for a long period of time to establish equilibrium initially. Near 100° equilibration occurred in a short period of time so that ΔH for the 50° interval of temperature could be established quite reliably. The individual heat capacity determinations were then used to construct a provisional curve of C_p *vs.* T. That curve was then adjusted upward proportionally so that the integrated heat effect obtained from the curve agreed with the directly measured ΔH for the 50 to 100° interval.

Results

The data for Mg_3Cd were obtained in 10 series of measurements involving a total of 81 determinations. For $MgCd_3$ there were 11 series and a total of 71 individual measurements. It was of course necessary to have the sample at equilibrium before and after each measurement. The treatment of the sample in the after-period has been described above. The details of the thermal conditioning of the samples prior to initiating a series of measurements are too numerous to relate here.[10] In general the thermal treatment was such that the sample was as near to equilibrium as could be achieved experimentally before measurements were begun. In some instances the treatment involved a very considerable amount of time and care. For example, with $MgCd_3$ below 80° it proved necessary to maintain the sample at temperature for roughly a week for it to come to equilibrium.

Smoothed values for the heat capacities are given in Table I. Excluding the regions of slow equilibration, the precision of the measurements is 0.1 to 0.2% as judged from the scatter of points from a smooth curve.

Residual Entropies.—Entropies of formation of magnesium–cadmium alloys were reported earlier based on measurements made using the electrochemical cell method.[3,11] The entropies of formation of $MgCd_3$ and Mg_3Cd at 270° were

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

(6) 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.

(7) J. C. Southard and F. G. Brickwedde, This Journal, **55**, 4378 (1933).

(8) Absolute constancy is of course never achieved. In practice because of stray voltages in the thermocouple circuits temperatures will steady off until there is a drift of 10^{-5} to 5×10^{-5} deg./min. With experience an operator can ascertain when a proper final state of the system has been reached.

(9) R. A. Flinn, R. S. Craig and W. E. Wallace, *J. Phys. Chem.*, **61**, 236 (1957).

(10) The details of the thermal preconditioning are given in ref. 5.

(11) F. A. Trumbore, This Journal, **76**, 5117 (1954).

TABLE I

HEAT CAPACITIES OF $MgCd_3$ AND Mg_3Cd

T, °K.	C_p, cal./deg. g. atom $MgCd_3$	C_p, cal./deg. g. atom Mg_3Cd	T, °K.	C_p, cal./deg. g. atom $MgCd_3$	C_p, cal./deg. g. atom Mg_3Cd
298.16	7.06	6.01	415	6.88	16.68
300	7.10	6.01	420	6.89	19.98
310	7.39	6.10	423.8	..	27.35
320	8.01	6.90			(max.)
330	9.05	7.00	425	6.89	18.02
340	10.88	7.16	430	6.90	7.40
345	12.41	7.25	440	6.91	7.10
350	13.95	7.35	450	6.93	7.03
355	16.28	7.47	460	6.95	6.99
357.0	21.04	..	470	6.98	6.96
	(max.)		480	7.00	6.94
360	9.19	7.59	490	7.02	6.93
365	7.46	7.72	500	7.04	6.94
370	6.98	7.87	510	7.07	6.97
380	6.90	8.23	520	7.10	6.93
390	6.88	8.70	530	7.13	6.94
400	6.88	9.41	540	7.17	6.98
405	6.88	9.91	543.16	7.18	6.99
410	6.88	12.23			

found to be 1.04 and 0.91 e.u., respectively.[12] Using the heat capacity data for the pure metals reported in the following paper[13] together with earlier data from this Laboratory for the low temperature region[14] 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 entropies of $MgCd_3$ and Mg_3Cd to be 16.14 and 13.65 e.u., respectively. The data in the present paper together with previously published results[3] permit the calculation of $S_{270°} - S_{0°K.}$ for the two compounds. These entropy increments are found to be 13.54 e.u. for Mg_3Cd and 15.96 e.u. for $MgCd_3$, from which one computes the residual entropies to be 0.11 and 0.18 e.u. for the respective compounds.

For reasons which shall now be indicated the quantities so computed represent that which may be called the uncorrected values. The compounds are formed upon cooling the corresponding magnesium–cadmium solid solution, the solution being the stable form at high temperatures. Since the transitions are second order and are spread out over a temperature range, progressive reduction of the temperature of the systems results in an accompanying configurational change. For the present purpose the configuration of the system can be represented by the Bragg–Williams[15] order parameter s. As temperature approaches 0°K., s tends to unity corresponding to the situation in which each magnesium atom occupies a magnesium site in the lattice and each cadmium atom, a cadmium site. However, in practice mobility is lost before perfect configurational order is achieved, s is frozen-in at some value slightly less than unity and the compound is left with a residual entropy.

The heat capacity data for Mg_3Cd show this freezing-in of the configuration in a very striking way (Fig. 1). The C_p values rise with temperature as if they will reach the Dulong–Petit limit at about 300°K. However, at about 310°K. there is a sudden rise in C_p followed by a small maximum, after which the heat capacity rises steadily until the λ point is reached. These results indicate that on cooling the order parameter becomes frozen-in at about 310°K. On warming back up configurational changes begin to occur at that temperature and there is a sudden rise in the heat capacity. The small maximum in C_p is undoubtedly a kinetic effect. Some of the configurational contribution which should have appeared at a slightly lower temperature has been displaced upward on the curve due to the slowness of atomic redistributions at the lower temperature. This point of view is supported by the results obtained by Welber, Webeler and Trumbore[16] using the continuous heating technique. Their results obtained with a heating rate of 4 deg./min. are also shown in Fig. 1. They find a small maximum at about 370°K. and their C_p values from 325 to 355°K. are about 10% lower than the present results. It seems clear that their technique delayed full development of the configurational contribution to C_p until temperatures in excess of 360°K. were reached at which point the mobility in the solid had increased to the point that the accumulated deficit in C_p could be realized. This gave rise to their maximum in C_p.

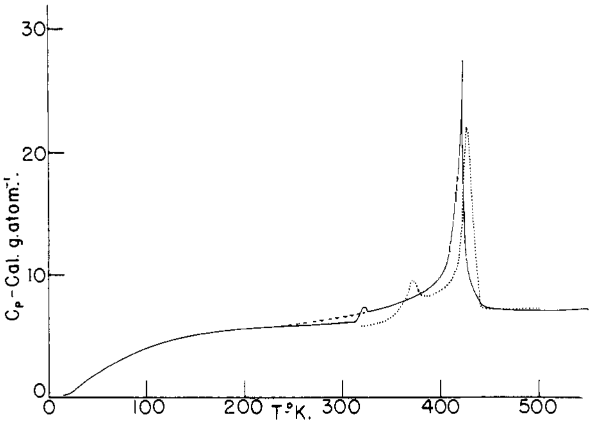

Fig. 1.—Heat capacity of Mg_3Cd: ——, this study; - - - - - -, present results corrected for frozen-in disorder (see text); . . . . . ., data of Welber, Webeler and Trumbore (ref. 16).

The dashed extension of the experimental curve in Fig. 1 shows the behavior to be expected if s had not become frozen-in. This extension has been constructed using results of theoretical treatments of order–disorder phenomena. The Bragg–Williams theory was used since results computed from their theory when s approaches unity do not differ from those obtained using more refined treatments. As s approaches unity, the configurational heat capacity C_p^c is given by the expression

$$C_p^c = \frac{\alpha}{T^2} e^{-\beta/T}$$

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[12] Data are expressed throughout this paper on a per gram atom basis. These data therefore refer to the entropy change accompanying the formation of one gram atom of alloy from the component metals.

[13] W. G. Saba, K. F. Sterrett, R. S. Craig and W. E. Wallace, THIS JOURNAL, **79**, 3637 (1957).

[14] R. S. Craig, *et al.*, *ibid.*, **76**, 238 (1954).

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

[16] B. Welber, R. Webeler and F. A. Trumbore, *Acta Met.*, **1**, 374 (1953).

where α and β are constants. C_p^c was estimated by extending linearly the curve below the sharp rise at 310°K. so as to join the curve at 530°K. and then subtracting data taken from this curve from the experimental results above the small maximum. A plot of log $C_p^c T^2$ *vs.* $1/T$ gave a linear plot over a 40° interval of temperature, but of course began to exhibit curvature at higher temperatures as s departed farther from unity. From the plot α and β were evaluated and the dashed extension in Fig. 1 was computed.

The corrected value of the residual entropy of Mg_3Cd was obtained by using the heat capacities given by the dashed extension instead of the measured values. When this is done and the best estimates of the uncertainties of the various quantities entering the calculation are made, one obtains as the corrected residual entropy of Mg_3Cd 0.03 ± 0.04 e.u. Thus within the limit of experimental error Mg_3Cd is found to obey the Third Law of Thermodynamics.

When the unsmoothed heat capacity data[3] for $MgCd_3$ were examined, it was found that there is a sharp rise and a small maximum at about 200°K. These are smaller than the ones shown in Fig. 1 for Mg_3Cd and had escaped notice at the time of the original publication. A procedure similar to that which was used for Mg_3Cd was applied to $MgCd_3$. The frozen-in disorder corresponded to 0.02 e.u., which leads to a corrected value for the residual entropy of 0.16 ± 0.04 e.u. for $MgCd_3$. The probable origin of this entropy will be considered in a later section of this paper.

Standard Heats, Free Energies and Entropies of Formation at 25°.—Values for all of these quantities have been reported earlier[4,11] for 270°. Using the present heat capacity data it is possible to calculate values for these quantities for 25°. Results of such calculations are shown in Table II. For Mg_3Cd the results pertain to the hypothetical state in which there is the equilibrium value of the order parameter s. In other words for this material the heat capacities used below 310° were not the data obtained experimentally but those taken from the dashed extension in Fig. 1. Although this is the way the calculations were made, the actual data might have been employed without incurring errors exceeding the listed uncertainties. Those uncertainties are rough estimates based upon the uncertainties in the various measured quantities employed in making the calculations. The principal contribution to the uncertainty in ΔH_f and ΔF_f is the uncertainty in the value of these quantities as measured at 270°. The uncertainties in the heat capacity data make a negligible contribution to uncertainty of those quantities but account for about half of the uncertainty in the ΔS_f values.

TABLE II

STANDARD HEATS, FREE ENERGIES AND ENTROPIES OF FORMATION OF $MgCd_3$ AND Mg_3Cd AT 25°

	$MgCd_3$	Mg_3Cd
ΔH_f (cal./g. atom)	−1130 ± 60	−1330 ± 50
ΔF_f (cal./g. atom)	−1177 ± 55	−1286 ± 45
ΔS_f (e.u./g. atom)	+ 0.16 ± 0.02	− 0.15 ± 0.02

Buck, Wallace and Rulon measured ΔH_f for these substances at 25° using a differential solution calorimetric technique.[17] They obtained −1595 and −775 cal./g. atom of compound for $MgCd_3$ and Mg_3Cd, respectively. These data are in poor agreement with the quantities given in Table II. The present data are undoubtedly more reliable. There are two reasons for believing that this is the case. First, as was pointed out earlier,[17] the directly determined ΔH_f's are extremely sensitive to experimental error. An error of 0.001 in mole fraction leads to an error of 180 cal./g. atom in ΔH_f and a weighing error of only 0.1 mg. affected ΔH_f to the extent of 450 cal. Second, there is a better appreciation now of the care which must be taken to establish equilibrium in the samples at 25°. It is possible that in the earlier study there was a considerable amount of frozen-in disorder in the samples of Mg_3Cd accounting for the large discrepancy in that case. The present results should be free of this difficulty since the electrochemical cell work was carried out at temperatures ranging from 270 to 300° where configurational equilibrium is quickly and easily established. Furthermore, sufficient attention was given to maintaining equilibrium during the heat capacity work that it is felt that no significant errors are introduced from this source into the data in Table II.

Discussion of Results

Heat Capacities.—The heat capacities reported in this paper join smoothly with the results obtained earlier[3] for the low temperature region. In addition to the work of Welber, *et al.*, referred to earlier, Nagasaki, Hirabayashi and Nagusa[18] and more recently Rosenbaum and Welber[19] have studied alloys with compositions fairly near to Mg_3Cd. The continuous heating technique was used in these studies. Their results resemble qualitatively the behavior exhibited in Fig. 1 except that the low temperature peak does not appear. However, because of the composition difference a detailed quantitative comparison seems unwarranted. Khomyakov, Kholler and Troshkina[20] have measured the heat capacity of a magnesium–cadmium alloy with composition which is stated to be 75.15 atomic % cadmium, also using continuous heating. Their results agree within about 3% with the present results up to 75°. Their specific heats reached a maximum at 77.7° whereas the present results continue to rise and reach a peak 25% higher at 83.9°. At 160°, the highest temperature reached by Khomyakov, *et al.*, the results again agree within a few per cent. The discrepancy between the temperatures at which C_p peaks in these two cases is in the wrong direction to be ascribed to kinetic factors. It must arise because the composition of the sample studied by Khomyakov deviated from 75.0 atomic % cadmium by

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

[18] M. Hirabayashi, S. Nagasaki, H. Maniwa and H. Nagusa, *J. Jap. Inst. Met.*, **13**, 1 (1949).

[19] B. M. Rosenbaum and B. Welber, *J. Chem. Phys.*, **24**, 485 (1956).

[20] 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).

more than the published composition would indicate, since Stepanov and Kornilov[21] have shown that the transformation point is maximal for the composition $MgCd_3$ and falls away for alloys whose cadmium contents are either greater or less.

The present study serves to emphasize the great care which must be exercised to obtain equilibrium heat capacities in systems which are undergoing atomic rearrangements. It is clear that the conventional continuous heating technique may in these cases lead to results which are seriously in error. Only if diffusion is exceptionally rapid, such as in beta brass, will the results be meaningful. For reasons which have been set forth earlier spurious heat capacity maxima can appear. (This to a lesser degree may also happen with the intermittent heating procedure.) Furthermore the heat capacity distribution under the λ-point for the continuously heated sample may be seriously distorted from its equilibrium shape. Thus, some aspects of the intense theoretical work of the 1930's dealing with order–disorder phenomena seems like effort misplaced. Much theoretical work was done in attempts to account for the exact temperature dependence of experimental configurational heat capacities, when due to the experimental method employed, the results obtained are now open to question.

Residual Entropy of $MgCd_3$.—As was shown earlier, even after allowing for frozen-in disorder associated with interchanged Mg and Cd atoms, $MgCd_3$ has a residual entropy of 0.16 e.u./g. atom of alloy. It is suggested that this entropy originates with vacant lattice sites (Schottky defects) which persist in this system down to the lowest temperatures studied. The density of $MgCd_3$ has been found[22] to be 1.7% less than that computed[23] from the unit cell dimensions. This density discrepancy has been attributed to the fact that an average of 1.7% of the lattice sites are unoccupied in $MgCd_3$. The special factors which lead to such an abundance of Schottky defects in this substance and which account for the fact that they are not removed on cooling are discussed elsewhere.[24,25] If it is assumed that the observed number of defects is randomly distributed over the lattice sites, the computed entropy is 0.17 ± 0.01 e.u./g. atom of alloy. This is, of course, in excellent agreement with the observed value.

It is appropriate to inquire about the results of a corresponding treatment for Mg_3Cd. Its measured density agrees with that computed from the unit cell dimensions within experimental error (0.2%). Therefore, one expects no residual entropy in this compound.

The low temperature at which the configuration freezes in and the small correction for frozen-in disorder for $MgCd_3$ are both suggestive of extensive vacancies in this substance at low temperatures. Atomic interchanges most likely occur through a mechanism involving a series of interchanges with a vacancy. The persistence of mobility to such low temperatures and low amounts of disorder is consistent with the notion that extensive vacancies exist in this system at low temperatures.

Acknowledgment.—The assistance of W. G. Saba in making a number of the calculations included in the work is gratefully acknowledged.

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[21] N. I. Stepanov and I. I. Kornilov, *Anni. secteur anal phys-chim., Inst. chim. gen (U. S. S. R.)*, **10**, 97 (1938).

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

[23] D. A. Edwards, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 5256 (1952).

[24] W. E. Wallace, *J. Chem. Phys.*, **23**, 2281 (1955).

[25] R. A. Flinn, R. S. Craig and W. E. Wallace, *J. Phys. Chem.* **61**, 234 (1957).

PITTSBURGH 13, PA.

[CONTRIBUTION NO. 1009 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Heat Capacities of Magnesium and Cadmium between 20 and 270°[1]

BY W. G. SABA, K. F. STERRETT, R. S. CRAIG AND W. E. WALLACE

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Heat capacities of magnesium and cadmium are reported for the temperature interval 20 to 270°. Measurements were made using an adiabatic calorimeter. Results are compared with previous determinations in the same temperature range. Deviations from the values accepted in the compilations by Kelley and Stull and Sinke are substantial for magnesium. For cadmium they are smaller but still appreciable. Results are in good agreement with the data obtained at lower temperatures by Craig, *et al.*

In making the thermodynamic calculations reported in the preceding paper[2] it was necessary to know the heat capacities of magnesium and cadmium in the temperature interval 25 to 270°. Values obtainable from the literature were not sufficiently precise, particularly for the residual entropy calculations, and so it became necessary to redetermine these quantities. The results of those redeterminations are reported in this paper.

Experimental Details

The apparatus employed and method of measurement have been described elsewhere.[3-5] The procedure employed in the present work differed from that used in the study of the magnesium–cadmium compounds only in that for some of the measurements on magnesium the individual determinations covered somewhat larger temperature intervals

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[1] This work was supported by a grant from the Atomic Energy Commission.

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

[3] W. V. Johnston, Ph.D. Thesis, University of Pittsburgh, August, 1955.

[4] W. E. Wallace, R. S. Craig and W. V. Johnston, U. S. Atomic Energy Commission Report No. NYO-6328, October, 1955. This document is available from the U. S. Government Printing Office.

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