largely remove the sodium component from the fusion product the hydrogenation of benzene will proceed. A noteworthy exception to this generalization is the 1 *N* $HNO_3$ leach described in Tables II and IV.

It was found that some of the modified[8] preparations would effect the hydrogenation of benzene alone, but the results were erratic and could not be correlated with sodium content.

One aim of this work was realized in the preparation of Catalyst F, Table IV. All preparations of this sodium-free, partially dehydrated platinic acid, stoichiometrically $PtO_2{\cdot}H_2O$, effected the hydrogenation of benzene alone. (Platinic acid, stoichiometrically $PtO_2{\cdot}4H_2O$, was not active as a catalyst for the hydrogenation of benzene alone or in the presence of acetic acid.) The object of preparing $PtO_2{\cdot}H_2O$ by the method of Wohler was to obtain a sodium-free material similar to Adams fusion product by an independent method. Unfortunately the $PtO_2{\cdot}H_2O$ prepared in this way cannot be said to be structurally similar to the fusion product because repeated X-ray powder diffraction studies of the former failed to yield any pattern indicative of crystallinity. However the $PtO_2{\cdot}H_2O$ can be considered a precursor of a product similar to the fusion product (*i.e.*, $PtO_2$) since its diffraction pattern indicates that it slowly assumes a like structure on heating at 350°. The fact that two substances of possibly very different structure effect hydrogenation similarly is not surprising since the oxides undergo a partial reduction and an evident change in physical appearance as they are reduced by the hydrogen prior to the hydrogenation of the acceptor. For example, analyses of one batch of fusion product before and after reduction in methanol showed the following platinum contents: fusion product, 78.5%; after reduction and washing in methanol, 94.4%. Commonly the catalysts after use are pyrophoric whereas the fusion product and the dehydrated platinic acid are unreactive toward the atmosphere.

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KNOXVILLE, TENNESSEE

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# Magnesium–Cadmium Alloys. V. Low Temperature Heat Capacities and a Test of the Third Law of Thermodynamics for the MgCd Superlattice[1,2]

BY C. B. SATTERTHWAITE, R. S. CRAIG AND W. E. WALLACE

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The heat capacities of an alloy containing 50.52 atomic per cent. cadmium between 12 and 300°K. are presented. From these data the entropy increase between 0°K. and 25°C. is computed and an estimate of the residual entropy for the superlattice (intermetallic compound) MgCd made. The alloy deviates negatively from the Kopp–Neumann rule below 200°K., where the configuration is frozen-in. At temperatures of 230°K. and above a transformation is observed. This has been established as the beginning of the order–disorder transition, which culminates in destruction of the superlattice at 528°K. In the temperature range where the configuration is changing, positive deviations from the Kopp–Neumann rule are observed. Debye characteristic temperatures are presented for the alloy, the equivalent mixture and the pure component metals.

## Introduction

In the preceding papers of this series results of determinations of (1) the densities and atomic volumes at 25°,[3] (2) heats, free energies and entropies of formation between 270 and 300°,[4] (3) heats of formation at 25°[5] and (4) certain crystallographic data[6] for the binary system magnesium–cadmium have been presented. The present paper contains results of measurements of the heat capacity of an alloy having a composition near to MgCd (actually 50.52 atomic per cent. cadmium) from 12 to 300°K. From these data and the entropy of MgCd obtained earlier in this Laboratory using the electrochemical cell the residual entropy of the MgCd superlattice can be calculated. The heat capacities have also been used together with data in the following paper for the pure metals (1) to ascertain the degree of conformity with the Kopp–Neumann rule for additivity of heat capacities at temperatures so low that the configuration is frozen-in and (2) to study the effect of temperature and composition on the Debye characteristic temperature.

## Experimental

**General Aspects of the Calorimetric Assembly.**—The calorimeter used was similar in principle to that employed by Southard and Brickwedde.[7] It was arranged so that it could be mounted either in a conventional cryostat using liquid nitrogen or solid carbon dioxide as a refrigerant for experiments at 80°K. or above or in the Collins Helium Cryostat for experiments below 80°K.

The design of the calorimeter differed appreciably from the conventional type of adiabatic calorimeter in only three respects: (1) the arrangement of certain components, especially the "thermal trap" and "floating ring," was altered so as to permit use of the Collins machine, (2) the customary sample container was replaced by a solid cylinder of the metallic sample in the center of which was a "core" containing the thermometer and heater and (3) the electric timer was operated by current generated by a calibrated tuning fork

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[1] From a thesis submitted by Mr. C. B. Satterthwaite in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, January, 1951.

[2] This work was assisted by the Office of Naval Research and the Atomic Energy Commission.

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

[4] F. A. Trumbore, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 132 (1952); paper II.

[5] T. M. Buck, Jr., W. E. Wallace and R. M. Rulon, *ibid.*, **74**, 136 (1952); paper III.

[6] D. A. Edwards, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 5256 (1952); paper IV.

[7] J. C. Southard and F. G. Brickwedde, *ibid.*, **55**, 4378 (1933).

since earlier work had shown[8] the local power supply to have a variation in frequency that was larger than the present experiments would permit. The essential features of the apparatus are shown in Fig. 1. A complete description of all experimental details is given elsewhere.[9]

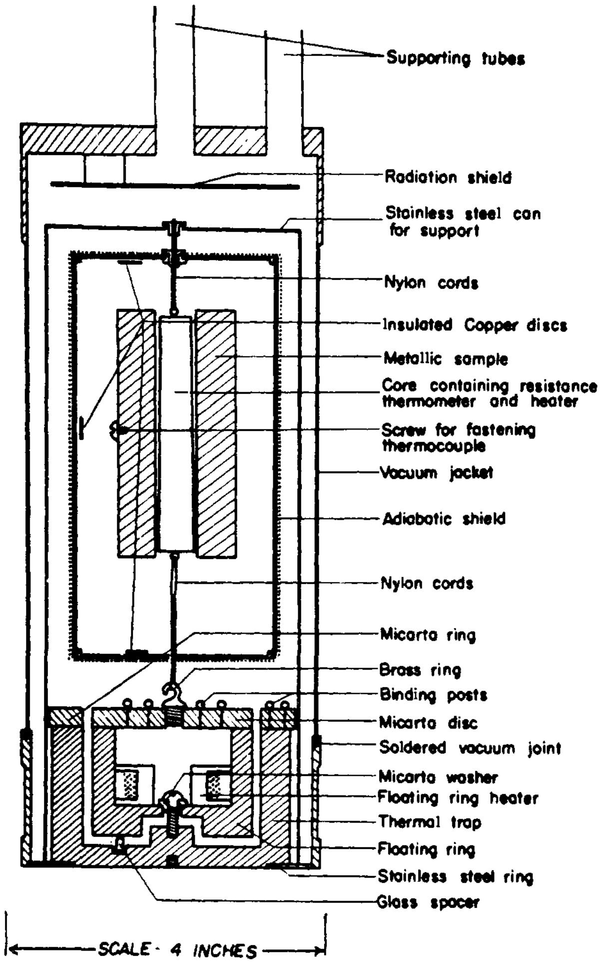

Fig. 1.—Calorimeter assembly.

**Core and Sample Mounting.**—The core, shown schematically in Fig. 2, was an integral unit containing the platinum resistance thermometer and the heater. The external monel casing was machined to the taper of a #9 taper pin reamer, 0.518 in. in diameter at the smaller end, 0.580 in. at the larger and 3 in. long. A $^7/_{16}$-in. hole was drilled along the axis from the larger end leaving $^1/_{16}$ in. of solid material at the smaller end. This hole was enlarged for $^7/_8$ in. at the larger end to give a wall thickness of 0.020 in.

A copper insert fitted snugly into the hole extending from the point of enlargement to $^1/_4$ in. from the smaller end. A heater of #36 enameled and silk covered constantan wire with a resistance of approximately 110 ohms was wound in spiral grooves cut in the outside of the insert and baked on with Pedegree varnish. The thermometer was soldered with Woods metal into a hole along the axis of the insert after the insert had been soldered into the casing with soft solder.

The leads from the thermometer and heater extended into the enlarged space at the larger end of the casing. These were soldered to #36 enameled and silk covered copper wires which were wound on a small copper spool soldered inside the casing near the larger end. The purpose of this spool was to bring the leads to the temperature of the sample to prevent heat loss along the lead wires during heating periods.

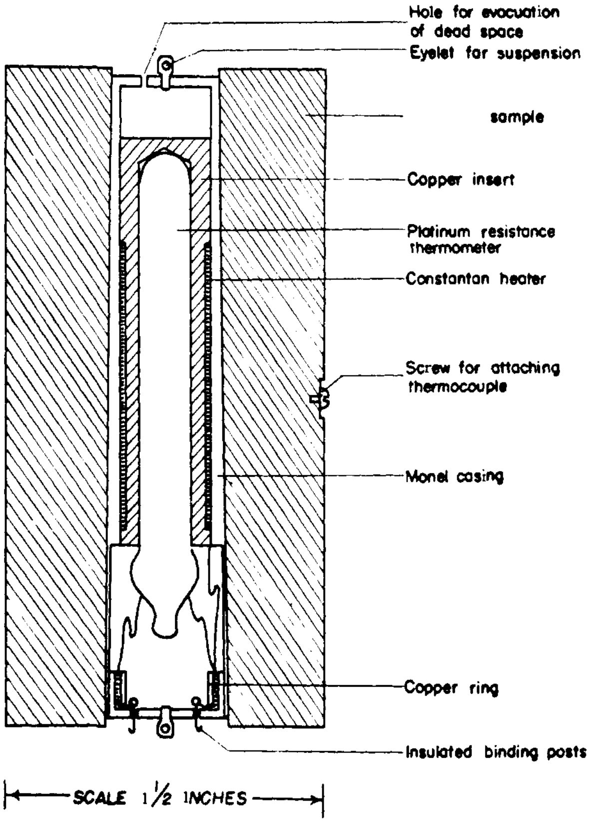

Fig. 2.—Cross section of sample with core containing thermometer and heater.

The leads from the spool were soldered to small insulated copper binding posts extending through a copper disk which was soldered into the large end of the casing.

Eyelets were screwed into either end of the core for suspension and holes were drilled in either end to allow for evacuation of the dead spaces.

The metallic sample was in the form of a cylinder 1.5 in. in diameter and $3^1/_8$ in. long with a hole along the axis reamed to the taper of the core so that, when mounted, it extended $^1/_{16}$ in. beyond the core at either end. The sample and core were suspended so that the weight of the sample rested on the taper. A weighed amount of "Apiezon N" stopcock grease was used to assure good thermal contact between the core and sample. A small steel screw was threaded into the side of the sample to which was fastened one junction of a difference thermocouple used to control the temperature of the adiabatic shield.[10]

**Thermal Trap and Floating Ring.**—The thermal trap and floating ring are standard parts of the conventional adiabatic calorimeter. The thermal trap is in contact with the refrigerating bath and serves to trap any heat flowing down the leads. The floating ring is thermally insulated from its surroundings and its temperature adjusted to approximately that of the shield. This serves to bring the leads to the shield temperature so that no thermal gradients develop in the shield due to contact with the leads.

The ring and trap are conventionally placed above the adiabatic shield and fastened in some way to the top of the vacuum jacket. Previous experiments in this Laboratory indicated that this design is not satisfactory for use in the Collins Helium Cryostat because of non-uniformity of temperature in the cold chamber. Consequently the parts were placed below the shield in this calorimeter where the thermal trap was in direct contact with liquid helium in the cryostat.

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(8) R. S. Craig, C. B. Satterthwaite and W. E. Wallace, *Anal. Chem.*, **20**, 555 (1948).

(9) C. B. Satterthwaite, Ph.D. Dissertation, University of Pittsburgh, 1951.

(10) This design is satisfactory for samples, like MgCd, whose thermal conductivities are good but is unsatisfactory for poor heat conductors. This sample holder was abandoned after attempts to use it to measure $C_p$ of cadmium. The new holder is described in the following paper.

The thermal trap and floating ring were both constructed of copper in the shape of heavy walled cups. The floating ring was mounted inside the thermal trap and was thermally insulated from it by means of glass spacers. The temperature of the floating ring was controlled by means of a heater. The arrangement of these parts may be seen in Fig. 1.

Twenty-eight #36 enameled and silk covered copper wires were wound on the outside of the thermal trap in such a way as to cover the surface with a single layer of windings. These passed through a hole in the wall of the thermal trap and were similarly wound on the floating ring. They were baked onto the ring and trap with Pedegree varnish to assure good thermal contact. These wires were soldered at one end to insulated binding posts on the thermal trap and at the other to similar binding posts on the floating ring. The wires extending out of the calorimeter assembly to the external electrical equipment were connected to these wires at the binding posts on the thermal trap. To the binding posts on the floating ring were connected wires leading to the adiabatic shield and to the thermometer and heater enclosed therein.

**Measurement of Time.**—A 60-cycle tuning fork (Type 815, supplied by the General Radio Co.) was used to generate the current which operated an electric clock. The frequency of the fork was determined by comparing a clock driven by the fork with time signals broadcast by the National Bureau of Standards. The time intervals of comparison were 1 to 1.5 hours. The frequency was found to be 59.986 ± 0.002 cycles/sec. at 25°. This value differed insignificantly from the frequency given by the manufacturer.

**Temperature Scale.**—The establishment of a Laboratory temperature scale between 10°K. and room temperature was accomplished using a Leeds and Northrup capsule type platinum resistance thermometer which had been calibrated at the National Bureau of Standards. This primary standard was compared with several other similar thermometers, one of which served as the working thermometer in the calorimeter, in the range between 10 and 90°K. The working thermometers were calibrated above 90°K. by determining their resistances at the oxygen, ice and steam points. These three fixed point calibrations served to determine both the three constants in the Callendar equation and the four constants in the Van Dusen equation, since, as Stimson has shown,[11] the constants $\beta$ and $\delta$ in the latter equation are related.

$$\beta = 0.58528\delta - 0.76222$$

Further details concerning the establishment of the temperature scale, including the rather elaborate interpolative procedure needed below 90°K., are given elsewhere.[9]

**Materials Employed.**—The magnesium and cadmium were donated by the National Lead Co. and the Anaconda Copper Mining Co., respectively. The donors represented the metals as being exceptionally pure. They were each analyzed in two ways. Conventional chemical analysis showed a purity in each case of 99.9% or better. Spectroscopic analyses also were made. Only traces of impurities were found amounting to an estimated total of less than 0.01%.

**Preparation, Analysis and Heat Treatment of Sample.**—The alloy was prepared by melting the two pure metals together using induction heating. A steel crucible having a graphite liner machined from a spectroscopically pure graphite rod was employed. During the melting the crucible was surrounded by an inert atmosphere of helium purified by evaporation from liquid helium. Details of the operation and construction of the furnace have been reported elsewhere.[9]

The alloy was maintained in a molten state for about 0.5 hr. after which it was cast, still under an atmosphere of purified helium, in a copper mold. A solid cylinder of alloy approximately 1.75 in. in diameter and 3.5 in. long was produced. The cylinder was machined to the dimensions of a calorimeter sample and portions were removed for analysis at points where the greatest differences in composition due to solidification were expected.

Analyses were made by the method described in an earlier paper.[4] Six analyses gave a composition of 50.52 ± 0.04 atomic per cent. cadmium. These determinations were made on the unannealed sample and since they gave no indication of inhomogeneity no further analyses were made.

The machined cylinder was sealed into a Pyrex tube containing about 1/2 atm. of purified helium and placed in a furnace at 325° for 10 days for further homogenization and the relief of strains. The temperature of the furnace was lowered to 225°, held there for 2 days and then gradually reduced to room temperature. The heat treatment at 225° and below was for the purpose of developing the superlattice which appears[12] on cooling at about 250°. After these heat treatments a very thin cut was taken with the reamer to assure a smooth taper. The mass of the alloy was the 433.099 g. or 6.293 g. atoms, using 112.41 and 24.32 for the atomic weights of cadmium and magnesium, respectively.

## Experimental Results

**Calibration of the Core.**—The heat capacity of the sample holder is customarily obtained by making measurements on the empty container. This procedure was not feasible in the present study since the calorimetric assembly did not function properly without a sample. To establish the heat capacity of the core a cylinder of cold rolled bar copper weighing 241.528 g. was fitted on the core and a complete set of heat capacity data was taken from 12 to 300°K. This cylinder was then removed, machined off until it weighed 117.384 g., returned to the calorimeter and a second series consisting of 28 determinations was made. These were not a complete set of data for while they included temperatures from 12 to 292°K., the data were bunched on the temperature scale with large intervals between them. From the two sets of data heat capacities of copper as cold rolled bar were calculated and compared with Giauque and Meads' results[13] on single crystals of copper. Expressed as average deviations between 50 and 300° K. they found that their heat capacities exceeded those of copper in the form of cold rolled bar by 0.018 cal. deg.$^{-1}$ mole$^{-1}$ which agrees very closely with 0.017 cal. deg.$^{-1}$ mole$^{-1}$, the corresponding difference between Giauque and Meads' and the present results.

To obtain the heat capacity of the core Giauque and Meads' results were employed first to construct a deviation plot using the 28 determinations referred to above and then were utilized along with the deviation plot to obtain a complete representation of specific heat *vs.* temperature for the particular sample of cold rolled copper bar used. The heat capacity of the core was then readily evaluated, knowing the specific heat of the copper used, from the first series of measurements on copper, which covered the entire range.

During the process of calibration the scheme just outlined seemed entirely satisfactory. Later it was realized that at the time of calibration the precision of the present equipment had been underestimated. It was found that the precision of the heat capacities warranted a better calibration since errors in calibration were the limiting factor. However, by that time it had been decided for other reasons to abandon the present sample holder and recalibration then did not seem worth the effort.

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(11) Private communication from Dr. H. F. Stimson of the National Bureau of Standards.

(12) Unpublished measurements of D. A. Edwards, J. D. Phillips, W. E. Wallace and R. S. Craig in this Laboratory. This transition was inferred earlier by thermal analysis, *e.g.*, G. Grube and E. Schiedt, *Z. anorg. allgem. Chem.*, **194**, 190 (1930).

(13) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941).

Errors due to calibration introduced less than 0.1% error into the heat capacities measurements above 125°K. but at lower temperatures the effect increased to 0.3% at 30°K. and 5% at 12°K.

**Heat Capacities of the Alloy.**—A heat capacity measurement consists in an initial rating period, a heating period and a final rating period. During the initial rating period temperature is measured at minute intervals for 5 to 10 minutes to see that the adiabatic control is functioning properly. Then an accurately measured quantity of electrical energy is introduced and a final rating period is taken to ascertain when thermal equilibrium is re-established and to verify again the effectiveness of the adiabatic control. Usually the temperature is either exactly constant or varies by a barely measurable amount during the rating periods, so that the heat capacity is obtained by dividing the energy input by the temperature rise during the heating period. Appreciable drifts of temperature during the rating periods are abnormal.

The behavior of the alloy was quite normal in the temperature range from 10 to 230°K. and measurements were made in a routine fashion. At approximately 230°K., however, slight upward drifts in temperature during the rating periods were noticed. These drifts were of the order of 0.0001°/min. and were at first attributed to slight differences in temperature between the shield and the sample due to stray electromotive forces in the difference thermocouples. As the temperature was increased the rates of drift increased to a maximum of approximately 0.0003°/min. at about 10 degrees below the ice point. At higher temperatures the rate decreased with increasing temperature until at approximately the ice point a downward drift was noticed. There the temperature seemed to be approaching a limiting value exponentially with time. As the temperature was increased beyond this point, the initial slopes of the downward drifts became steeper and the leveling off to constant temperature more rapid. At 35° temperature equilibrium was reached after an experiment so rapidly that the behavior was again considered normal.

This behavior seemed to indicate that a transformation of some sort was taking place in the alloy, the transformation extending over a considerable range of temperature. Two experiments were devised to check this supposition. The first was to heat over widely differing temperature intervals in approximately the same region of temperature and observe the behavior after heating in each case. Both heating periods were started at the ice point using an ice-bath in the cryostat. One covered a 2-degree interval and the other a 10-degree interval. The initial slope observed after the 10-degree heating period was much steeper than that observed after the 2-degree period but the time required to reach a constant temperature was approximately the same in each case. The rates of heating were the same in both instances so no difference in behavior due to temperature equilibration would be expected.

In the second experiment the sample was cooled rapidly and its time–temperature behavior was observed after the cooling to test the reversibility of the phenomenon. This was done by first raising the temperature of the sample about 25 degrees above that of the ice-bath while maintaining the calorimeter under vacuum. Rapid cooling was achieved by breaking the vacuum with helium. When the temperature had dropped approximately 10 degrees, the helium was pumped out and a vacuum again obtained. The adiabatic shield and floating ring were adjusted to the temperature of the sample. Temperature measurements were started before the sample had stopped cooling so initially a steep downward drift was observed. The temperature of the sample reached a minimum and started to increase, rapidly at first but at a rate which seemed to decrease exponentially with time. A plot of temperature *vs.* time gave a curve very closely resembling a freezing curve where supercooling has occurred. Since the cooling occurred at the surface of the sample and since the thermometer was located in the center, the observed rise in temperature can only result from the generation of heat in the sample.

These experiments essentially verified the supposition that a reversible transformation was taking place. They also showed that the rate of this transformation was such that equilibrium could be virtually attained (at least over part of the temperature range in which the transformation occurred) by extending the time of the rating periods.

In a later section it will be shown that the transformation observed at and above 230°K. is probably the slow beginning of the second-order transition which results in the destruction of the superlattice at 528°K. For each temperature there is in the superlattice an equilibrium degree of disorder which vanishes at the absolute zero. Actually, the hypothetical perfectly ordered superlattice is never realized since at some temperature the mobility becomes so low that the disorder characteristic of that temperature is frozen-in and no change takes place with further cooling. The first series of heat capacity measurements indicated that the freezing-in temperature for MgCd lies in the vicinity of 230°K. From these measurements one could see that although some mobility persisted to 230°K., equilibration was a fairly slow process at all temperatures below room temperature. Extremely long equilibration times at temperatures near 230°K. were accordingly expected.

With these factors in mind a second series of determinations of heat capacities between 200 and 300°K. was made using a procedure designed to permit the alloy to attain equilibrium insofar as possible in the initial cooling and between determinations. Between 200°K. and the ice point solid carbon dioxide was used in the cryostat. The sample was cooled very slowly from room temperature to the temperature of the cryostat in order to maintain the sample at equilibrium to as low a temperature as possible. The slow cooling was accomplished by maintaining the system under vacuum while the cryostat was at solid carbon dioxide temperatures. Under these conditions approximately 24 hr. was required to reach the cryostat temperature. Above the ice point an ice-bath was used in the cryostat and equilibrium was attained at the bath temperature by allowing the sample to remain at that temperature for 2 days.

After the sample was heated time–temperature readings were taken until equilibrium was attained, when feasible, throughout this series of determinations. In the range from approximately 230 to 260°K. the transition was so slow that it was impossible to attain a constant temperature after the addition of heat. In fact, in this temperature region it was impossible to detect a change in the slope in the time–temperature curve such as would occur as equilibrium was approached. Measurements in this range were, therefore, rather uncertain. It was of interest to note that these data when plotted joined smoothly with reliable data at either end of the questionable range of temperature. This showed that the contribution of the transformation to the heat capacity was quite small between 230 and 260°K. and negligible error was incurred due to failure to maintain equilibrium in this region.

The smooth data are presented in Table I. These data are based on 93 individual determinations, a few of which were discarded because of obviously non-equilibrium conditions, so taken as to cover the entire temperature range; that is, the final rating period of one experiment was the initial rating period of the next one. The region below 60°K. was covered completely twice, with different cooling rates from room temperature, and there was no detectable difference in results. As indicated earlier the region above 200°K. was also covered twice. All of the discarded data were in this range and from the first series when slow cooling was not employed. The time sequence was such that once a series was begun, experiments were performed continuously until the series was concluded.

TABLE I

ATOMIC HEAT CAPACITIES OF THE ALLOY

| Temp., °K. | $C_p$,[a] cal./deg. g. atom | Temp., °K. | $C_p$,[a] cal./deg. g. atom |
|---|---|---|---|
| 12 | 0.102 | 130 | 5.004 |
| 13 | .137 | 140 | 5.139 |
| 14 | .179 | 150 | 5.258 |
| 15 | .226 | 160 | 5.360 |
| 17.5 | .369 | 170 | 5.451 |
| 20 | .536 | 180 | 5.531 |
| 25 | .980 | 190 | 5.603 |
| 30 | 1.276 | 200 | 5.667 |
| 35 | 1.626 | 210 | 5.724 |
| 40 | 1.950 | 220 | 5.774 |
| 45 | 2.252 | 230 | 5.819 |
| 50 | 2.534 | 240 | 5.866 |
| 60 | 3.049 | 250 | 5.914 |
| 70 | 3.484 | 260 | 5.963 |
| 80 | 3.860 | 270 | 6.014 |
| 90 | 4.175 | 280 | 6.068 |
| 100 | 4.438 | 290 | 6.125 |
| 110 | 4.663 | 298.16 | 6.173 |
| 120 | 4.848 | 300 | 6.186 |

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

**Entropy Change between 0°K. and 25°C.**—The gain in entropy above 12°K. was evaluated by graphical integration of the data in Table I to be 9.80 e.u./g. atom. The $T^3$ law was assumed to hold below 12°K. From it $\Delta S$ accompanying the increase in temperature to 12°K. was computed to be 0.03 e.u./g. atom. Hence

$$S_{25^\circ\text{C.}} - S_{0^\circ\text{K.}} = 9.83 \text{ e.u./g. atom}$$

**Precision of Experimental Quantities.**—To facilitate observation of the deviations of the individual $C_p$ measurements from a smooth curve the temperature range covered was divided into six intervals, $C_p$ was analytically related to temperature by a linear function and the deviation between calculated and observed $C_p$ plotted *vs.* temperature. This procedure constitutes merely a means of expanding the $C_p$ scale. A smooth curve was then drawn through the deviation points and the scatter observed. From these the average % deviation of $C_p$ from a smooth curve was found to be 0.8, 0.05 and 0.02 in the ranges 12–30, 30–80 and 80–300°K., respectively. These random errors do not include systematic errors due to calibration referred to earlier.

The precision of the entropy at 25° is estimated to be ±0.1% or less.

## Derived Results

**Experimental Results and the Kopp–Neumann Rule.**—Statistical treatments of solid solutions are usually simplified by assuming[14] that the vibrational characteristics are independent of configuration, for in this way the partition function can be factored into vibrational and configurational contributions. On this basis the vibrational specific heat is independent of configuration. In case of a solid solution which is isomorphous with its components, the difference between the solution and its separate components is merely one of configuration. Hence, their heat capacities are assumed to be the same and the solution is said to obey the Kopp–Neumann rule.

The Kopp–Neumann rule is widely used in metal physics because few reliable heat capacity data for alloys exist. That the rule has neither a theoretical nor an experimental basis seems insufficiently appreciated. The data presented in this paper permit a clear indication of its limitation for this one alloy. According to the rule, $\Delta C_p$, the change in heat capacity accompanying alloy formation is zero. Table II shows $\Delta C_p$ for the alloy at various temperatures.

TABLE II

$\Delta C_p$ OF FORMATION

| Temp., °K. | $\Delta C_p$, cal./deg. g. atom | Temp., °K. | $\Delta C_p$, cal./deg. g. atom |
|---|---|---|---|
| 20 | −0.133 | 150 | −0.056 |
| 40 | − .043 | 200 | − .022 |
| 60 | − .081 | 250 | .005 |
| 80 | − .100 | 300 | .101 |
| 100 | − .088 | | |

The $\Delta C_p$ values in Table II show that for this system there is considerable departure from the Kopp–Neumann rule. The large positive deviations above 200°K. may be explained as contribu-

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

tions to the heat capacity of the alloy due to the order–disorder transition which, of course, are not present in the pure metals. Below 200°K., however, the alloy may be considered quite normal and representative of alloy systems so that a valid test of the Kopp–Neumann rule may be made. Deviations in this range amounted to as much as 20% of the total heat capacity.

The entropy at 25° obtained by assuming the Kopp–Neumann rule differs from that obtained from measured heat capacity values by approximately 0.20 e.u./g. atom.

There are instances reported in the literature where the entropy changes associated with the formation of alloys have been measured at room temperature or above and corrected to 0°K., using the Kopp–Neumann rule, to obtain a residual entropy for use in estimating residual disorder in the alloy system. It is not unusual to find a residual entropy of as little as 0.05 e.u./g. atom resulting from such a computation and being used to estimate residual disorder. In view of the departures from the Kopp–Neumann rule noted with the cadmium–magnesium system any residual disorders estimated in the fashion described must be regarded as open to question.

**Constant Volume Heat Capacities and the Debye Characteristic Temperatures.**—$C_v$ at 25° was computed from the thermodynamic relationship $C_p - C_v = \alpha^2 TV/\beta$ using $66 \times 10^{-6}$ (°C.)$^{-1}$, 12.8 cm.$^3$ and $2.18 \times 10^{-6}$ atm.$^{-1}$ as the thermal expansivity,[15] atomic volume[3] and compressibility,[16] respectively. $C_v$ values at lower temperatures were computed from the empirical formula $C_p - C_v = AC_p^2T$, where $A$ was evaluated from the data for 25° to be $1.63 \times 10^{-5}$ g. atom/cal. Results at several temperatures are shown in Table III.

Table III

Constant Volume Heat Capacities of MgCd and Debye Characteristic Temperatures

| $T$, °K. | $C_v$, cal./deg. g. atom | Mg | Cd | $\theta$, °K. MgCd (mixture) | MgCd (alloy) |
|---|---|---|---|---|---|
| 12 | 0.102 | 368 | 126 | 156 | 198 |
| 15 | .226 | 361 | 128 | 161 | 190 |
| 20 | .536 | 351 | 134 | 174 | 188 |
| 25 | .908 | 338 | 139 | 185 | 192 |
| 50 | 2.529 | 322 | 159 | 225 | 228 |
| 100 | 4.406 | 323 | 170 | 249 | 254 |
| 150 | 5.190 | 319 | 179 | 235 | 254 |
| 200 | 5.563 | 309 | 194 | 236 | 236 |
| 250 | 5.771 | 297 | 215 | 258 | 200 |
| 300 | 5.999 | 267 | 228 | 249 | Negative |

The $C_v$ values in Table III may be used to evaluate a Debye characteristic temperature $\theta$ at each temperature. The scatter of the $\theta$'s so obtained is a simple and sensitive indication of the ability of the Debye theory to account for the experimental results. The variation of $\theta$ shown in Table III is in line with that observed for other solids[17] and emphasizes again the inability of the Debye model to account for all details of a precise heat capacity curve. For comparison purposes $\theta$'s for the two pure metals obtained in the following paper[18] are also presented in Table III along with $\theta$'s for the mixture equivalent to the alloy. These latter $\theta$'s are, of course, the ones which the alloy would have if it obeyed the Kopp–Neumann rule. $\theta$ for the alloy can also be calculated from the elastic constants. The value so obtained[16] is 220°K.

The rapid drop in $\theta$ for the alloy above 200°K. is due to the additional heat capacity resulting from the transformation occurring in that temperature region. The negative value at 300°K. merely indicates that the total has exceeded the Dulong–Petit value of $3R$.

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

Earlier an account was given[4] of the determination of the heats, free energies and entropies of formation of magnesium–cadmium alloys using the electrochemical cell method at temperatures between 270 and 300°. From that study[19]

$$0.5\text{Mg(s)} + 0.5\text{Cd(s)} = 0.5\text{MgCd(s)} \quad \Delta S_1 = 1.09 \text{ e.u.}$$

for 270°. The entropy change at 25° can be evaluated from the known[20] specific heats of the pure metals between 25 and 270° and the recently published[21] specific heats of MgCd in this temperature range.

$$0.5\text{Mg(s, 25°)} = 0.5\text{Mg(s, 270°)} \quad \Delta S_2 = 1.92 \text{ e.u.}$$
$$0.5\text{Cd(s, 25°)} = 0.5\text{Cd(s, 270°)} \quad \Delta S_3 = 1.94 \text{ e.u.}$$
$$0.5\text{MgCd(s, 25°)} = 0.5\text{MgCd(s, 270°)} \quad \Delta S_4 = 5.08 \text{ e.u.}$$
$$0.5\text{Mg(s)} + 0.5\text{Cd(s)} = 0.5\text{MgCd(s)} \quad \Delta S_5 = -0.13 \text{ e.u.}$$

where $\Delta S_5$ is for 25°.

Using the value for entropies of cadmium and magnesium at 25° presented in the following paper,[18] the absolute entropy of MgCd at 25° can be calculated.

$$S_{\text{Mg}}(25°) = 7.78 \text{ e.u./g. atom}$$
$$S_{\text{Cd}}(25°) = 12.37 \text{ e.u./g. atom}$$
$$S_{\text{MgCd}}(25°) = \Delta S_5 + \frac{S_{\text{Mg}} + S_{\text{Cd}}}{2} = 9.95 \text{ e.u./g. atom}$$

This last figure is to be compared with $S(25°) - S(0°\text{K.})$ for MgCd from the low temperature specific heat measurements. The experimental results apply to the alloy containing a slight excess of cadmium. Correction to an exactly equimolal alloy can be made with the aid of the Kopp–Neumann rule. Table II indicates that except at the lowest temperatures the heat capacity of the alloy is additive to better than 5%. This is the case when 50% of the atoms are replaced in the lattice. To go from an alloy of composition 50.52 to 50.00% requires a replacement of about 0.5% of the atoms. If the deviation from the

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(15) M. Hirabayashi, S. Nagasaki, H. Maniwa and H. Nagasu, *J. Jap. Inst. Met.*, **13**, 6 (1949).

(16) Charles S. Smith and W. E. Wallace, *J. Chem. Phys.*, **21**, 1120 (1953).

(17) R. H. Fowler and E. A. Guggenheim, *ref.* 14, p. 146.

(18) R. S. Craig, C. A. Krier, L. W. Coffer, E. A. Bates and W. E. Wallace, This Journal, **75**, 238 (1953).

(19) When this paper was in galley proof form, an error in calculation was discovered in the work reported in ref. 4. A note of correction will be published later in This Journal. The entropy data in this and paper VII of the series are the corrected values.

(20) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Academic Press, Inc., New York, N. Y., 1951, p. 218.

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

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

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

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

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

and

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

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-

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(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).