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.

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

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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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(10°). This was possible because the heat capacities were almost linear with temperature. In contrast with the behavior observed when the compounds were being studied the calorimeter came to thermal equilibrium in the normal length of time (about 30 min.) throughout the temperature range covered.

The samples employed were portions of samples used in the study of the low temperature specific heats of these metals published earlier.[6] The masses of the samples used were: magnesium, 127.613 g. or 5.2472 g. atoms; cadmium, 639.451 g. or 5.6886 g. atoms.

Results

For magnesium thirty-seven determinations were made covering the range 20 to 275°. The data for cadmium consisted of 39 measurements extending from 27 to 280°. The smoothed heat capacities obtained are given in Table I. The average deviation from a smooth curve drawn through all the points was 0.12 for magnesium and 0.08 for cadmium, indicating a precision of about 0.1%. Of the 76 results only 9 deviated from the smooth curve by more than 0.2%. The maximum deviations were 0.4% and 0.35% for magnesium and cadmium, respectively.

TABLE I

HEAT CAPACITIES OF MAGNESIUM AND CADMIUM

T, °K.	C_p, cal./deg. g. atom Magnesium	Cadmium	T, °K.	C_p, cal./deg. g. atom Magnesium	Cadmium
298.16	5.941	6.212	430	6.314	6.556
300	5.948	6.218	440	6.339	6.586
310	5.982	6.239	450	6.363	6.616
320	6.013	6.259	460	6.386	6.652
330	6.042	6.283	470	6.414	6.692
340	6.072	6.307	480	6.440	6.728
350	6.104	6.334			
360	6.134	6.361	490	6.467	6.769
370	6.163	6.390	500	6.493	6.814
380	6.189	6.416	510	6.517	6.869
390	6.216	6.443	520	6.541	6.927
400	6.241	6.470	530	6.561	6.988
410	6.266	6.499	540	6.583	7.054
420	6.289	6.527	543.16	6.591	7.076

It is of interest to compare the present data with results obtained in earlier studies. Kelley[7] and Stull and Sinke[8] have reviewed existing heat capacity data for these two elements and have accepted certain values as the best representation of their heat capacities for the above room temperature range. Their accepted values coincide for cadmium but differ appreciably for magnesium. Both accepted values for magnesium deviate on the average from the present results by about a per cent.; Kelley's equation leads to a result which is very much too low at the low temperature limit (4% at 300°K.). Agreement with the present data is somewhat better for cadmium. Between 300 and 500°K. the deviations average 0.22%, but above 500°K. the differences rapidly increase until at 540°K. the accepted results computed from Kelley's equation are low by 2.4%. Examination of the original literature, and limiting consideration to the last 25 years, reveals that cadmium has been studied by Bronson and Wilson[9] (−80 to 120°) and magnesium has been studied by Jaeger and Poppema[10] (0 to 550°) and Seekamp[11] (18 to 500°). As was the case in the earlier study of cadmium at lower temperatures the results of Bronson and Wilson are in good agreement with those obtained in this Laboratory. Over the 90° interval of temperature common to both series of determinations the maximum deviation is 0.22% and the average deviation is 0.15%, Bronson and Wilson's results being consistently higher by this amount. Seekamp's data for magnesium scatter about the present results; the deviations average about 0.8% and rise to a maximum of 1.1%. Jaeger and Poppema's results are consistently lower than those reported in this paper by about 0.7% but the difference in no case exceeds 0.9%.

Low temperature heat capacities of magnesium and cadmium were determined[6] in this Laboratory several years ago covering the range 12 to 320°K. In the 20 degrees of overlap it is found that the present results are consistently about 0.2% lower than the previous results. Since the two sets of data were obtained using entirely different instruments, this difference is perhaps indicative of the combined systematic error present in the measurements. Considering the deviations normally observed between independently determined heat capacities, this close agreement between the two sets of data is gratifying.

The rather rapid rise of the heat capacities of cadmium above the equation of Kelley for temperatures in excess of 500°K. has been mentioned above. This appears to be the beginning of a heat capacity anomaly associated with premelting, or heterophase fluctuations,[12] such as have been observed for the alkali metals.[13] Khomyakov, *et al.*,[14] have studied pure cadmium in the immediate vicinity of the melting point. They find a sharp rise in the heat capacity curve and claim that more than one third of the normally reported latent heat of fusion is associated with this premelting heat capacity anomaly. The rapidly increasing slope in the curve obtained in this study for cadmium above 500°K. represents perhaps the faint beginnings of the more pronounced effects observed by Khomyakov, *et al.*, above 570°K. In contrast, the curve for magnesium near the upper limit of the present study appears to be leveling off, which is not surprising since this substance is still so far removed from its melting point that any influence of heterophase fluctuations on its heat capacity is expected to be slight.

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