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Magnesium–Cadmium Alloys. II. The Use of the Electrochemical Cell to Determine the Heats, Free Energies and Entropies of Formation of the Solid Alloys in the Temperature Range Above the Order–Disorder Curie Points[1,2,3]

BY FORREST A. TRUMBORE, W. E. WALLACE AND R. S. CRAIG

The cell Mg(s)/Mg^{++} (in LiBr–RbBr)/Mg[in Cd(s)] was employed to determine the changes in heat content, free energy and entropy accompanying the formation of solid magnesium–cadmium alloys at temperatures ranging from 270 to 300°. All the alloys are formed exothermally with a maximum in the heat evolved being 2.02 kcal./g. atom at 42%[4] magnesium. The alloys are formed with a release of free energy at all compositions and the variation of free energy with composition indicates a stable single phase system over the entire composition range. An entropy increase accompanies the formation of all the alloys. A comparison of the observed entropy with the ideal entropy of mixing shows a pronounced deficiency for alloys having compositions around 50%. This has been attributed to the existence of short range order. An entropy excess occurs in the cadmium-rich alloys. Explanations for the anomalous entropy excess can be provided by postulating the existence of vacant lattice sites to the extent of 2 to 3% and/or an exceptionally large degree of vibrational freedom in high-cadmium alloys. The latter possibility seems to be a likely one in view of the difference in packing in the two pure metals as suggested by their strikingly different axial ratios. Rough correspondence between the observed results and those expected from the quasi-chemical theory were noticed, although such correlations are probably of dubious significance as the volume of the alloys does not obey the additivity relationship and the packing varies with composition.

Introduction

This paper describes one of a series of investigations currently underway in this Laboratory to study and correlate the structures and chemical thermodynamics of solid binary alloys. The magnesium–cadmium system was one of the systems chosen for intensive study since it exhibits for an appreciable range of temperature (260 to 320) complete miscibility in the solid state.[5] Also as this range of temperature is immediately above the order–disorder Curie point for MgCd (258°), it seems likely that the alloys at these temperatures retain a considerable degree of short range order. Thus this system offers an excellent opportunity to study (a) the variation of thermodynamic properties as a function of composition over the entire composition range in a single homogeneous phase and (b) the influence of short range order on the thermodynamic behavior of these alloys.

The large difference in electronegativity of magnesium and cadmium, together with the high degree of mobility[6,7,8] in their alloys, makes it possible to study this system in the reversible electrochemical cell: Mg(s)/Mg^{++} (in LiBr–RbBr)/Mg[in Cd(s)]. Measurements to date have been confined to the temperature interval extending from 270 to 300°. The upper limit of temperature has been imposed by the volatility of cadmium, while the lower limit was fixed by the eutectic temperature of the LiBr–RbBr system. To the present time it has not been possible to operate the cell at temperatures below 270°, where the long range order begins to appear, because of the lack of a suitable solvent.[9]

Experimental

Method Employed.—The experimental features and treatment of data necessary to obtain information pertaining to the thermodynamics of alloying using the electrochemical cell have frequently been discussed.[10,11] The special precautions which must be observed when dealing with solid alloys have been emphasized by Wachter.[12] In practice one fashions a cell of the type

$$A/A^{n+}(\text{in solution})/A(\text{in an AB alloy})$$

where A is the least noble of the two metals and the cell solvent is some inert material capable of dissolving at least a few per cent. of the ions of A. In the present work A is, of course, magnesium.

From the voltage developed the free energy of A in the alloy relative to that of pure A is obtained. Knowing these free energies as a function of alloy composition the relative free energy of B is computed from the Gibbs–Duhem–Margules relationship. The free energy of formation ΔF_f for one gram atom of alloy may then be computed from the expression[13]

$$\Delta F_f = N_A(\bar{F}_A - F_A^0) + N_B(\bar{F}_B - F_B^0) \qquad (1)$$

By repeating this procedure at several temperatures the temperature coefficient of ΔF_f can be established and the heats and entropies of formation of the alloys evaluated.

Choice of Solvent.—It has been the usual practice to employ fused salt mixtures as solvents in cells having alloy electrodes[11] since a degree of mobility in the alloys sufficient to permit reversible cell behavior is normally realized only at somewhat elevated temperatures. The extreme reactivity of magnesium, together with the particular temperature region of stability of the disordered alloys, imposed severe restrictions on the salts that could be employed in this study. The eutectic melt of LiBr–RbBr seemed promising as a solvent. Preliminary investigation indicated that the eutectic temperature for this system lies between 265 and 270°. Furthermore, it was sufficiently inert to the cell

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[1] From a thesis submitted by Mr. Forrest A. Trumbore in partial fulfillment of the requirements for the Doctor of Philosophy degree at the University of Pittsburgh, September, 1950.

[2] The first paper in this series appeared in *J. Phys. Colloid Chem.*, **52**, 999 (1948).

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

[4] Percentages will in all cases signify atomic percentages.

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

[6] N. I. Stepanov, *et al.*, *Compt. rend. acad. sci. U. R. S. S.*, [N.S.], **4**, 147 (1935); *Ann Secteur anal. phys.-chim.*, *Inst. chim. gen.* (*U. S. S. R.*), **10**, 78 (1938); *ibid.*, **10**, 97 (1938).

[7] I. I. Kornilov, *Compt. rend. acad. sci. U. R. S. S.*, **19**, 157 (1938); *Bull. acad. sci. U. R. S. S.*, *Class. sci. math. nat.*, *Ser. chim.*, 313 (1937).

[8] The observations of Stepanov, Kornilov, *et al.*, are supported by unpublished results from this Laboratory. Heat capacity determinations between 200 and 300°K. have revealed an anomaly in this region. The structural changes responsible are quite sluggish at 200°K. but become reasonably rapid near the ice point, judging from the behavior of the calorimetric equipment.

[9] Very recently a solvent of LiBr-RbBr-CsBr has been employed. Preliminary indications are that with this solvent the cell can be operated down to temperatures at least as low as 235° and perhaps to 220°. Data for the lower temperatures will be presented in a later paper.

[10] C. Wagner, "Handbuch der Metallphysik," Vol. I, Pt. 2, 1940, p. 80.

[11] F. J. Dunkerley and G. J. Mills, "Thermodynamics in Physical Metallurgy," American Society for Metals, Cleveland, Ohio, 1950, p. 47.

[12] A. Wachter, THIS JOURNAL, **54**, 4609 (1932).

[13] The notation is that employed by G. N. Lewis and M. Randall "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

electrodes and, of course, dissolved sufficient magnesium ion. Consequently, throughout this study a LiBr–RbBr melt, containing between 50 and 55 weight per cent. RbBr, was used as a solvent.

Materials Used.—The magnesium was obtained from two sources, the National Lead Company and the Dow Chemical Company, while the cadmium was supplied by the Anaconda Copper Mining Company.[14] All samples were analyzed spectroscopically and were found to be free of metallic impurities to within 0.02 to 0.05%. No further purification was attempted.

Magnesium bromide was prepared by dissolving pure magnesium in hydrobromic acid and recrystallizing from aqueous solution. Lithium and rubidium bromides were prepared by treating the C.P. carbonates with hydrobromic acid and evaporating to dryness.

The salt mixture used as a solvent in the cell was prepared by fusing together lithium and rubidium bromides to which had been added a few per cent. of magnesium bromide. Some recrystallized ammonium bromide was also added to the mixture prior to fusion to suppress hydrolysis. The molten salt mixture was poured into a cup made of purified magnesium and the final drying was completed *in situ* in the cell by maintaining the solvent in the molten state for a period of several hours under high vacuum at a temperature of about 300. During this final drying period the magnesium cup acted as a "getter" for water, oxygen and any other traces of impurities in the electrolyte capable of irreversible reaction with magnesium.

Preparation, Heat Treatment and Analysis of Alloys—The alloys were prepared by fusion of the metals in a graphite crucible (turned from a rod of spectroscopically pure graphite) and were cast in a copper mold all under an inert atmosphere of purified argon or helium. The alloys as cast were in the form of rods about 1 cm. × 5 cm. which were then anealed under an inert atmosphere at temperatures of from 300 to 325° for a period of two to five weeks. This treatment served to insure both physical and chemical homogeneity judging from the reproducibility of chemical analyses and potentials obtained using different sections of the same alloy.

The alloys were analyzed by converting a known amount of alloy to magnesium and cadmium sulfates and weighing the mixture. The validity of this method was confirmed by performing analyses on known magnesium–cadmium mixtures. The accuracy of the method depended somewhat on the composition of the alloy or mixture being analyzed. The uncertainty in composition was ±0.0002 in the mole fraction for the most favorable range of composition and ±0.001 for the least favorable range.

Cell Design.—From preliminary experiments it was evident that scrupulous care was necessary to prevent (1) the entry into the cell of contaminants capable of reacting irreversibly with the extremely reactive hot magnesium and (2) thermal gradients. Failure on either of these accounts led to an improperly functioning cell.

The exclusion of contaminants once the cell was assembled was simple. One merely arranged to have the cell completely enclosed so that the surrounding space could either be evacuated or filled with an inert gas. The latter procedure was adopted on account of the volatility of cadmium. The inert gas was extremely pure helium produced by evaporating liquid helium. The exclusion of contaminants prior to or during the assembly of the cell was more difficult. Absorption of water by the extremely hygroscopic LiBr–RbBr mixture made it necessary to complete the dehydration of the solvent *in situ*, as referred to earlier. Of course, it was necessary to withhold the electrodes from the solvent during the final drying period. This was accomplished by incorporating in the vacuum system a windlass by means of which the electrodes could be lowered into the solvent at the appropriate time without opening the gas-tight system.

The elimination of thermal gradients was accomplished by proper thermostating and by shaping the electrode so that the portion of the alloy projecting above the solvent had a very small cross-sectional area.

The cell and thermostat assembly was fabricated from a 4-in. brass rod, into which was drilled a centered hole $1^1/_2$ in. × 6 in. The magnesium cup containing the solvent fitted snugly into the bottom of this hole. A water-jacketed stainless steel tube was hard soldered into the mouth of the $1^1/_2$ in. hole. The other end of the stainless steel tube was connected, by means of a wax joint, to a glass tube provided with (1) a large standard taper glass joint for introducing the electrode assembly and (2) a connection for evacuating and flooding with helium.

A heating coil was wound on the outside of the brass rod. The unit as a whole was placed in a crock one ft. in diameter and the annular space was filled with a thermal insulator.

The temperature was controlled manually by means of a variable transformer whose primary was fed by a constant voltage source. A thermocouple well was drilled in the brass rod and temperatures were measured with an iron–constantan thermocouple standardized at the tin and lead points. The correspondence between temperatures in the cell and in the thermocouple well was examined in a separate experiment. Using a difference thermocouple a constant difference of 0.5 to 0.6° between the well and cell temperatures was found. The recorded temperatures were accordingly reduced by that amount.

Provisions were made for accommodating seven electrodes in the cell of which three were magnesium reference electrodes.

Procedure.—After the final fusion of the electrolyte, the electrodes were lowered into the melt and helium was admitted to the cell. A period of several hours was allowed to elapse for the cell to attain electrical and thermal equilibrium. A group of electromotive force observations was taken as valid when both the temperature and electromotive force remained relatively constant for one or two hours. The total time required to determine the temperature dependence of the electromotive force for a group of alloys varied from two weeks to a day, depending upon the nature of the alloys.

Special measures were necessary for alloys containing more than 90% cadmium. The voltages for these alloys showed a tendency to decrease with time, indicating a preferential loss of cadmium from the surface of the electrodes. This effect was not unexpected in view of the volatility of cadmium. Several steps were taken to reduce the importance of this vaporization. (1) The size of these electrodes was increased by a factor of three to four over that of the other electrodes to reduce the effect of the loss of a small amount of cadmium. (2) The time during which evaporation could occur was reduced drastically by taking data very rapidly, although this involved some uncertainty in the individual measurements. (3) No attempt was made to obtain data at temperatures higher than 285° since the complications associated with the vaporization losses increased with temperatures. Thus it was necessary to use extrapolations to obtain data for the higher temperatures with the possibility of again introducing error. (4) Instead of seven electrodes, only four were used including three of pure magnesium. In this way the separation of alloy and reference electrodes was increased, thereby reducing the chance of contaminating the reference electrodes with evaporating cadmium. (5) Chemical analyses were performed on the electrodes actually used in the cell rather than on separate sections as was the case for the other compositions. This latter measure was probably of little importance since in alloys of high cadmium content, voltage changes so rapidly with composition that an appreciable change in voltage could result from an undetectable change in composition. One of these high cadmium alloys was analyzed *before* and *after* use in the cell and no change in composition was observed within the limits of experimental error of the analysis.

Experimental Results

Judging from the constancy of the voltages developed the cell employed in this study was extraordinarily well behaved. In all cases the observed voltages were constant to considerably better than 0.1 mv. It was not unusual to find a cell developing a voltage constant to within 0.003 mv. over a period of several hours. These highly reproducible voltages were obtained only after the cell had been maintained in the temperature range between 270 and 300° for several hours. At first the potentials

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[14] Thanks are due to Dr. L. A. Carapella formerly of the National Lead Company, Mr. A. D. Brooks of the Dow Chemical Company and Mr. R. B. Caples of the Anaconda Copper Mining Company for the donation of the metals used in the present series of investigations.

were rather erratic, probably indicating a period during which strains were disappearing.

During the experiments a close watch was kept over the potential differences existing between the three pure magnesium reference electrodes. Normally these voltages were less than 0.03 mv, and occasionally they were as low as 0.002 mv. When the reference electrodes exhibited abnormally large voltages, some sort of mechanical failure was suspected and usually found. These "blank" voltages served as a rather effective criterion for satisfactory cell behavior. In a few cases, particularly those involving alloys of high cadmium content, blank voltages as large as 0.1 mv. were observed.[15] It was thought that in such cases cadmium had distilled from the alloy to the reference electrodes.

TABLE I

VOLTAGES DEVELOPED BY THE CELL $Mg(s)/Mg^{++}/Mg$ [IN $Cd(s)$]

N_{Mg}	Electromotive force at 270°, mv.	dE/dT, mv./°C.
0.0054	200.5	0.275
.0506	144.9	.138
.0942	128.6	.097
.2527	91.36	.040
.4029	59.64	.0225
.5264	36.66	.019
.6098	24.50	.018
.7481	10.60	.013
.8891	3.25	.005
.9691	0.86	.0005

It is perhaps worth reporting that at no time was there any evidence of hysteresis in the voltage–temperature behavior. For the most part data were *not* taken in a regular progression from high to low temperature or *vice versa*. The sequence of measurements was planned so that time dependent effects might be accentuated.

In view of the magnitude of the blank voltages the measured potentials were regarded as reliable to 0.05 mv. Accepting this figure as the limit of reliability, plots of potential *versus* temperature at constant composition gave straight lines over the narrow range of temperature covered for all alloys studied. Consequently, the raw data can be summarized very compactly. This is done in Table I.

The activities and the partial molal free energies, heats and entropies of the magnesium were obtained directly from the data in Table I through the use of standard equations relating the electromotive force to these quantities. The corresponding values for cadmium were calculated by graphical integration of the Gibbs–Duhem equation. From the partial molal quantities, the total free energies, heats and entropies of formation were calculated in the usual manner.

The results of these calculations for 270° are given in Table II. Sufficient data are included to permit the evaluation of the corresponding quantities for other temperatures up to 300° with very little effort.

The linearity of the voltage–temperature curve means that $(\bar{C}_p - C_p^0)_{Mg} = 0$ within the limits of experimental error. Thus, $(C_p - C_p^0)_{Cd} = 0$ and the values for $\bar{S} - S^0$, $\bar{L}$, ΔH_f and ΔS_f are all independent of temperature over the temperature interval covered by the measurements. ΔF_f and the activities do vary with temperature. They can be evaluated from the expressions

$$\Delta F_f = \Delta H_f - T\Delta S_f$$

$$RT \ln a_M = \bar{L}_M - T(\bar{S} - S^0)_M$$

where M is either magnesium or cadmium.

TABLE II

THERMODYNAMIC DATA FOR SOLID MAGNESIUM–CADMIUM ALLOYS AT 270°

N_{Mg}	a_{Mg}	a_{Cd}	$\bar{L}_{Mg}$, cal./g. atom	$\bar{L}_{Cd}$, cal./g. atom	$(\bar{S} - S^0)_{Mg}$, E.U./g. atom	$(\bar{S} - S^0)_{Cd}$, E.U./g. atom	ΔF_f, cal./g. atom	ΔH_f, cal./g. atom	ΔS_f, cal./g. atom
0.000	0.000	1.000		0		0.00	0	0	0
.100	.0045	.6291	−3497	− 276	4.31	.41	−1034	− 598	0.80
.200	.0138	.3731	−3343	− 677	2.36	.71	−1775	−1210	1.04
.300	.0319	.2084	−2917	−1229	1.47	.85	−2300	−1735	1.04
.400	.0762	.1122	−2210	−1878	1.04	.89	−2527	−2011	0.95
.500	.1761	.0597	−1376	−2501	0.92	.99	−2457	−1938	0.96
.600	.3315	.0321	− 742	−2992	.83	1.32	−2199	−1642	1.02
.700	.5446	.0171	− 280	−3274	.69	2.05	−1775	−1177	1.10
.800	.7305	.0089	− 81	−3526	.47	2.89	−1290	− 768	0.96
.900	.8810	.0038	− 32	−3782	.19	4.10	− 723	− 404	0.58
1.000	1.000	.000	0		.00			0	0

Discussion of Results

Estimates of Precision.—The values for the heats, free energies and entropies of alloying given in Table II become more significant if some estimate of their reliability can be made. Rigorous objective estimates of precision are, unfortunately, not possible in this case. The mathematical operations involved, particularly the graphical integration and the extrapolation, permit only semi-quantitative estimates to be made.

Taking into consideration such factors as variation in cell potential, errors in measuring voltages, analysis errors, possible extrapolation errors, etc., the estimates of precision presented in Table III were obtained. Details of the considerations leading to these results are given elsewhere.[16] The inclusion of similar estimates for alloys having compositions other than 50% does not seem necessary

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(15) Large and erratic blank voltages were observed in the initial period while strains were being relieved and also in certain cases where the solvent appeared to be contaminated. If the alloy-platinum lead wire interface was allowed to come in contact with the solvent, large blanks were observed and there were many direct indications of corrosion.

(16) F. A. Trumbore, Ph.D. Dissertation, University of Pittsburgh, 1950.

as the absolute errors are maximal or nearly so for the equimolar alloy.

TABLE III

ESTIMATES OF PRECISION OF THERMODYNAMIC DATA FOR MgCd

ΔF_f	±10–20 cal./g. atom
ΔH_f	±50–75 cal./g. atom
ΔS_f	±0.02–0.04 E.U./g. atom
$(\Delta C_p)_f$	±2–3 cal./g. atom °C.

Heats and Free Energies of Alloying.—The general features of the composition dependence of these quantities are evident from Table II. The exothermal nature of the alloying of magnesium and cadmium agrees with previous thermal measurements made on this system. Details of the comparison of the results obtained by different investigators will be presented in a later paper. The observation that the alloys are formed with a release of heat is consistent with their development of superstructures at reduced temperatures.

The free energy behavior substantiates the observations of Hume-Rothery and Raynor[5] that at these temperatures the two metals are completely miscible in the solid state. It will be recalled that phase segregation can occur only when the curve showing ΔF_f *versus* composition is such that a line can be drawn which is tangent to the curve at two points,[17] the points of tangency giving the compositions of the two phases at equilibrium. No common tangent is possible for the present free energy data.

Entropies of Alloying.—The entropy changes associated with the formation of the alloys are represented graphically in Fig. 1 together with the ideal entropies of mixing. Two aspects of the entropy behavior merit comment—the pronounced dip midway along the composition axis and the excess entropy over that of ideal behavior (random mixing) in the cadmium-rich alloys.

It seems very likely that the decrease in entropy around mole fraction 0.5 is due to the existence of short range order. The persistence of local order above the order–disorder Curie point is a well established fact.[18] The explanation for the high entropy in the cadmium-rich alloys is less obvious. The excess over ideal entropy may be attributed to (a) extra vibrational entropy in the alloy relative to the pure metals, (b) the existence of vacant lattice sites in the alloy (Schottky defects) or (c) a combination of the two. Of these (a) and (c) seem more likely, as the existence of 2 to 3% vacant lattice sites must be postulated to account for the observed entropy behavior solely in terms of (b). The existence of so many lattice defects seems improbable but perhaps not impossible. Measurements are currently underway in this Laboratory to ascertain the fraction of lattice sites which are vacant in this system.

The occurrence of exceptionally high vibrational entropies in the alloys of high cadmium content appears to be a distinct possibility. From crystal structures studies it is known that the axial ratios in cadmium and magnesium differ considerably, 1.89 *versus* 1.63, the ratio for magnesium being the normal value for close packed spheres. The anomalous axial ratio in cadmium can be crudely viewed in terms of a cadmium ion having the shape of a prolate spheroid. In a like fashion the axial ratio for magnesium can lead one to regard the magnesium ion as a perfect sphere. Consider now the transfer of a magnesium ion from its own into a cadmium lattice. The spherical magnesium ion must fit itself into a space vacated by an ellipsoidal cadmium ion. Disregarding the restrictions imposed by relative ion sizes, the magnesium ion should enjoy considerably greater freedom in the cadmium lattice than in its own. Thus, on this basis the transfer process should be accompanied by an entropy increase.

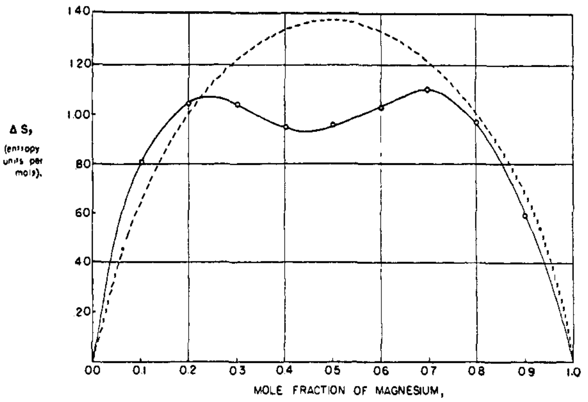

Fig. 1.—Plot showing the measured (—) and ideal (- - - -) entropies of formation of magnesium–cadmium alloys at 270°.

The difference in ion sizes, however, cannot be disregarded. The volume per ion in magnesium exceeds that in cadmium by roughly 5%. If for no other reason than this, the substitution of cadmium by magnesium must produce a disturbance extending over several atomic diameters. A quantitative evaluation of the influence of this disturbance on the vibrational entropy probably requires a keener insight into solid state physics than is to be had at this time. Qualitatively one might expect the vibrational entropy either to decrease due to the tightening up of the vibrational modes as the solute ion enters or to increase as a result of the general structure weakening effect of interchanging two such dissimilar particles. The volume characteristics[2] of this system clearly point to the predominance of the second factor. All alloys with compositions less than 90% are formed with a diminution of volume, as would be expected from the exothermal nature of the alloying process. Above 90%, however, there is a curious reversal in the volume characteristics of this system in that the volume of alloy *exceeds* that of the components. This strongly suggests considerable structure weakening in the high cadmium range. Similar inferences can be drawn from the small slope of the solidus curve on the cadmium end[5] and the remarkably rapid drop in axial ratio[6] as the magnesium content of the alloys is raised from 0 to 20%.

The possibility should not be overlooked that the extra entropy comes from the vibrational modes

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(17) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., p. 499.

(18) F. C. Nix and W. Shockley, *Rev. Mod. Phys.*, 10, 1 (1938).

and vacancies in the lattice. In the limiting case where mobility is quite high, it may be impossible to distinguish between these two sources of extra entropy conceptually or experimentally. Either effect to the exclusion of the other is an extreme whereas the actual state of affairs probably is somewhere in between.

Present Experimental Results and Theories of Alloying.—So far, theoretical treatments of the enegetics of alloying are in a primitive state of development. This situation exists not for any lack of attention but because of the formidable nature of the problem. The most elegant theory of non-ideal binary solutions which has appeared is the so-called quasi-chemical theory due to Guggenheim[19] and Rushbrooke.[20] This theory has been developed for what Fowler and Guggenheim call strictly regular solutions.[21]

Magnesium–cadmium alloys were examined to see if they could qualify as strictly regular solutions. If so, they would be of considerable interest as a test of the applicability of regular solution theory to metallic solutions. The small heats of formation (as compared to typical bond energies) indicate only moderate departures from ideal behavior. This is, of course, the kind of solution which is most useful for comparison with theory as these are just the ones which, next to ideal solutions, are most amenable to theoretical treatment.

Magnesium–cadmium alloys fail to qualify as strictly regular solutions in at least two important respects—the volume of alloys are not additively related to the volumes of the constituents and the large difference in axial ratios indicates a significant difference in packing in the two pure components. Failure to satisfy the volume requirements could be rectified by correcting to constant volume conditions. Unfortunately, the data necessary to make these corrections are not available. The packing differences referred to above represent a more fundamental limitation which probably cannot be simply overcome.[22]

In spite of these obvious deficiencies it was of interest to make comparisons between the experimental results and the behavior anticipated from theory. The quasi-chemical theory leads one to expect[23] heats and free energies of alloying which are symmetrical about mole fraction 0.5. Considering the limitations mentioned the results shown in Table II are in reasonably good agreement with the requirements of theory.

[19] E. A. Guggenheim, *Proc. Roy. Soc.* (*London*), **A148**, 304 (1935).

[20] G. S. Rushbrooke, *ibid.*, **A166**, 296 (1938).

[21] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," The Macmillan Company, New York, N. Y., 1939, p. 351.

[22] P. W. Bridgman (*Proc. Am. Acad. Arts Sci.*, **60**, 305 (1925)) has found several high pressure modifications of cadmium. The first new form appears at about 2800 atm. Dehlinger (*Z. anorg. allgem. Chem.*, **194**, 223 (1930)) regards this as the pressure at which the axial ratio of cadmium collapses to the normal value for close packed spheres. If this supposition proves to be correct, the differences in packing could be eliminated by correcting all data to this pressure region above 2800 atm. However, the problems associated with determining the necessary data for making these corrections (expansivities and compressibilities as functions of temperature and pressure) appear to be formidable indeed.

[23] A. Munster, *Z. physik. Chem.*, **195**, 67 (1950).

PITTSBURGH, PENNA.

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Magnesium–Cadmium Alloys. III. Some Calorimetrically Determined Heats of Formation at 25°[1,2]

BY THOMAS M. BUCK, JR., W. E. WALLACE AND RICHARD M. RULON

The heats of formation of several magnesium–cadmium alloys are presented. The results were obtained from the difference in heat of solution of the alloy and a mixture having the same mass and composition. A differential calorimeter was employed to measure the differences directly. The measured heats of formation at 25° are −1595 ± 60, −1960 ± 50, −2197 ± 70 and −775 ± 70 cal./gram atom of alloy for compositions 25.27, 49.50, 52.64 and 74.81% magnesium,[3] respectively. Comparisons are made with similar data from other investigations. Agreement is poor with older calorimetrically determined values but is reasonably satisfactory with the values obtained in this Laboratory using the electrochemical cell. Efforts to determine the energies associated with the formation of the magnesium–cadmium superstructures by comparing the heats of formation above and below the order–disorder Curie points were unsuccessful. Some experiments are reported dealing with the energetics of the hydrogen reduction of chloroplatinate and chloroplatinite ions, substances useful for accelerating the acid solution of metals, such as cadmium, which have high hydrogen overvoltages. Chloroplatinate ion, used in most of the classic work on the heat of solution of simple metals in acids, was found to be less satisfactory, in view of its reduction to two lower valency states, than chloroplatinite ion. Possible errors in published values of the heats of solution of the simple metals due to an incorrect accounting for the accelerator correction are mentioned. A rough value, useful in applying an accelerator correction, for the hydrogen reduction of chloroplatinite ion was obtained. At 25° this value is 0.21 ± 0.01 cal. per mg. of platinum deposited.

Introduction

In the investigation described in the preceding paper[4] (hereinafter referred to as II) the heats, free energies and entropies of formation of magnesium–cadmium alloys were determined using the reversible electrochemical cell. The present paper contains an account of the determination of the heats of formation of some of the same alloys by calorimetric means. The measurements reported in II were for temperatures above the order–disorder Curie points for the magnesium–cadmium system whereas the present measurements are for 25°, which is below the Curie points. Hence by intercomparing the two sets of results it was hoped that the superlattice energies might be evaluated.

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[1] From a thesis submitted by Mr. Thomas M. Buck, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh, August, 1950.

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

[3] Percentages throughout this paper are atomic percentages.

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