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.

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(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).

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[Contribution No. 822 from the Department of Chemistry, University of Pittsburgh]

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).

The calorimetrically determined heats of formation promised to be of additional interest in indicating the precision with which such quantities can be determined using modern calorimetric facilities and employing an alloy system free of the various difficulties associated with metastable states.

Experimental

Method Employed.—The method essentially amounted to the measurement of the difference in heat of solution in a suitable acid medium of an alloy of magnesium and cadmium and a mixture of the two metals having the same composition and total mass. This is, of course, a familiar technique for evaluating such thermal properties.[5] In the present study the heats of alloying were determined directly in a single experiment using a differential calorimeter. The solutions of the alloy and the mixture were simultaneously carried out in two portions of the calorimeter and the difference in heat of solution was evaluated, subject to certain minor corrections, by determining the electrical heat necessary to restore the relative temperatures in the two portions of the calorimeter to the value existing prior to the solution process. Temperature differences were measured electrically by a 25-junction copper–constantan difference thermel connected directly to a high sensitivity galvanometer.

Calorimetric Equipment.—The apparatus used was that constructed by Fineman and Wallace[6] for studying the energetics of alkali halide solid solutions. It was employed without modification with the exception that the crushing devices used to introduce the various salts in the earlier study were replaced by tantalum reaction chambers for carrying out the metal–acid reactions.

The sensitivity of the calorimetric equipment was such that 0.005 cal. in the differential heat of solution could be detected (the reproducibility was never that good) out of a total differential heat effect varying from about 0.9 to 4.2 cal. in these experiments. (The total heat evolved in the two portions of the calorimeter varied from 100 to 200 cal.).

The hydrogen produced in the experiments escaped through a tube $^1/_8$ in. in diameter and in contact with the calorimeter water for about an inch. Provisions for better heat exchange with the calorimeter water were not feasible with the calorimetric facilities available. It appeared that some errors might be introduced by the failure of the escaping hydrogen to communicate its heat to the calorimeter. A separate series of experiments was performed to evaluate this source of error.

In those experiments the escaping hydrogen was conducted into a small copper heat exchanger, cylindrical in shape and almost filled with a thimble type platinum resistance thermometer. The heat loss from the calorimeter was computed from the increase in temperature of the platinum resistance thermometer immediately following a metal–acid reaction. The validity of this procedure was confirmed by duplicating the experimental situation in all respects except that the hydrogen came from a bulb equilibrated in an auxiliary thermostat set at various temperatures above and below that of the chamber containing the platinum thermometer. (This procedure also served as a calibration of the platinum thermometer–copper cylinder assembly.) In this way it was found that a temperature differential of 2° could be detected. A series of experiments revealed that the hydrogen was escaping from the calorimeter at a temperature of 30 ± 2°.

In a typical experiment, therefore, a maximum of about 0.07 cal. was lost from each reaction chamber. This loss appeared to be constant, within the limits stated, for various metal–acid reactions so that in an actual heat of formation experiment the losses would cancel on the average to within perhaps 10% or 0.007 cal., which would constitute 0.2 to 0.7% of the final result. The loss of heat in the escaping hydrogen can therefore be neglected since errors from other sources considerably exceed these figures.

Preparation, Analysis and Heat Treatment of Alloys.—Three of the alloys studied were portions of the samples prepared for the electrochemical cell work. The method of preparation of these alloys is described in II. The other alloy (50.50% cadmium) was a portion of a large sample prepared for low temperature specific heat studies. The method of preparation was essentially identical with that used for the other samples in that the two pure metals were melted together by induction heating in a steel crucible having a graphite liner machined from a spectroscopically pure graphite rod. 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.[7]

The samples as cast were in the form of cylindrical bars. Following the homogenization heat treatment (described in II) samples were prepared for use in the calorimeter by filing or sawing the bulk specimens. There were two possible sources of contamination in the filing and sawing operations mentioned—atmospheric oxidation and metallic contamination from the file or saw. Colorimetric analyses for iron showed the latter possibility to be insignificant. Atmospheric corrosion was avoided by performing the filing and sawing operations in a "dry-box" under helium.[8] As the alloys are somewhat susceptible to atmospheric attack, they were kept out of contact with air after being removed from the dry-box up to the time of weighing out the sample for use in the calorimeter.

The filed or sawed samples were sealed off under purified helium and annealed at 250–300° overnight to relieve strains. In addition, the alloys were annealed at lower temperatures to effect the transformation into the ordered states known to exist at room temperatures. The annealing conditions for producing the superstructures were deduced from the kinetic studies of Stepanov[9] and Kornilov[10] dealing with the rates of formation of the ordered structures existing in this system. They were: $MgCd_3$—several weeks at room temperature; MgCd—12 hours at 200°; Mg_3Cd—4 hours at 110°. The times mentioned in all cases exceed by a factor of ten or more the minimum amount of time deemed necessary.

Accelerator Correction.—Aqueous HCl was chosen as the medium for use in the calorimeter. To achieve a rate of solution sufficiently rapid for satisfactory calorimetry when pure cadmium and the high cadmium alloys were employed some kind of accelerator was necessary. Richards[11] in his classic work on the heats of solution of metals in acids used H_2PtCl_6 as an accelerator in dealing with metals such as cadmium. The use of this accelerator introduces a side reaction

$$2H_2 + PtCl_6^{=} \longrightarrow Pt + 4H^+ + 6Cl^-$$

for which a correction to the heat effect is necessary. Richards made the correction by weighing the platinum deposited and multiplying by a factor determined by Thomsen.[12]

It was decided to use H_2PtCl_6 as an accelerator in this work and as the correction might be rather important it appeared desirable to remeasure the heat effect associated with the side reaction. Preliminary results indicated a value exceeding Thomsen's by a factor of three or four if the amount of platinum deposited was taken as a measure of the extent of reaction. This was in time traced to the reduction of the unprecipitated platinum to chloroplatinite. At this point H_2PtCl_6 was abandoned as an accelerator in favor of H_2PtCl_4.[13]

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[5] F. Weibke and O. Kubaschewski, "Thermochemie der Legierungen," Julius Springer, Berlin, 1943.

[6] M. A. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

[7] C. B. Satterthwaite, Ph.D. Dissertation, University of Pittsburgh, February, 1951.

[8] Eugene E. Ketchen, F. A. Trumbore, W. E. Wallace and R. S. Craig, *Rev. Sci. Instruments*, **20**, 524 (1949).

[9] 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).

[10] 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).

[11] For a bibliography of T. W. Richards' work on the heats of solution of metals in acids see F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 444.

[12] J. Thomsen, "Thermochemische Untersuchungen," Vol. III, Barth, Leipzig, 1883, p. 284.

[13] The failure to include in the accelerator correction the appreciable heat effect associated with the reduction of chloroplatinate ion to chloroplatinite may have introduced significant errors into those determinations where chloroplatinic acid was used as an accelerator, as, for example, in Richards' work on the heats of solution of metals in acids.

TABLE I

HEATS OF FORMATION OF MAGNESIUM-CADMIUM ALLOYS AT 25°

Mole fraction of magnesium	Mass of sample, g.	Experimental heat effect, cal.	Accelerator correction, cal.	$-\Delta Hf$, cal./gram atom Single values	$-\Delta Hf$, cal./gram atom Mean	Systematic error due to ±0.001 in N_{Mg}, cal./gram atom
0.2527 ± 0.0009	0.13987	2.235	0.063	1439	1595 ± 60	∓135
	.10009	1.775	.231	1599		
	.12791	2.480	.336	1748		
	.10683	2.050	.473	1731		
.4950 ± .0002	.13240	3.580	.176	1861	1960 ± 50	∓180
	.11510	3.450	.060	2061		
	.11434	2.985	.162	1796		
	.12499	3.845	.374	2122		
.5264 ± .0007	.11999	3.470	.176	1910	2197 ± 70	∓180
	.12131	4.245	.071	2311		
	.12241	4.110	.119	2218		
	.10692	3.805	.110	2350		
.7481 ± .0003	.06207	0.935	.044	702	775 ± 70	∓285
	.07373	0.810	.121	513		
	.06199	1.335	.063	1001		
	.06426	1.220	.084	882		

The side reaction using H_2PtCl_4 as an accelerator is

$$H_2 + PtCl_4^{=} \longrightarrow Pt + 2H^+ + 4Cl^-$$

The heat of this reaction was estimated by inserting in the calorimeter a special reaction chamber[14] for carrying out the reduction. The heat of deposition of platinum from chloroplatinous acid solution was found to be −0.21 ± 0.01 cal./mg. of platinum.

The reaction chambers used to dissolve the metal samples were designed so that at the conclusion of an experiment the mixed chloride solution could be filtered to determine the quantity deposited. Correction for the side reaction was made by determining the difference in platinum deposited in the two portions of the calorimeter.

Experimental Results

Numerous preliminary experiments were performed before a procedure which seemed to be reasonably satisfactory was worked out. The final experiments, consisting of a group of sixteen individual determinations, are presented in Table I. For the most part the table is self-explanatory. The sample mass shown in Column 2 is the mass of alloy or mixture. The systematic errors listed in Column 7 indicate the constant errors introduced if the composition of the alloy was in error by an amount 0.001 in the mole fraction. The uncertainties listed are in all cases probable errors of the mean, p_m, and are computed from the expression

$$p_m = 0.6745\sqrt{\frac{\epsilon\delta^2}{n(n-1)}}$$

where δ = deviation of a single determination from the mean and n is the number of experiments.

Discussion of Results

It is obvious from Table I that the measurements of the heats of formation of this alloy system scatter appreciably. Even the probable error of the mean, always a flattering way of expressing the precision of a group of measurements, ranges from 3 to 10%. However, the precision of the present results can be regarded as rather satisfactory by comparison with the precision customarily attained in work of this kind, namely, one or more kcal./gram atom. It seems likely that the scattering of the present results is due largely to weighing errors as the measured heats of alloying are very sensitive to this kind of error. In the worst cases an error of 0.1 mg. in the mass of magnesium in the mixture introduces an error of 450 cal. into ΔH_f.

Apart from the random errors due to weighing, etc., the ΔH_f values must contain sizeable systematic errors due to the uncertainty in the composition of the alloy. This kind of error results from the fact that the weights of cadmium and magnesium in the mixture are ascertained from the sample weight and the analysis of the alloy. A bad analysis leads to systematically incorrect weights and consequently rather large systematic errors.

The results obtained in the present study are compared in Table II with those obtained in this Laboratory using the electrochemical cell and also with earlier calorimetric measurements by Biltz and Hohorst[15] and Roos.[16]

TABLE II

COMPARISON OF INDEPENDENTLY DETERMINED HEATS OF FORMATION OF MAGNESIUM-CADMIUM ALLOYS

	$-\Delta Hf$, cal./gram atom			
Mole fraction of magnesium	This study (calorimetric, 25°)	Trumbore, Wallace and Craig (electrochemical cell, 270°)	Biltz and Hohorst (calorimetric, 18°)	Roos
0.2527	1595 ± 60	1510		
.4950	1960 ± 50	1950		
.5000			4600	8900
.5264	2197 ± 70	1910		
.7481	885 ± 70	950		

The earlier calorimetric measurements appear to be of interest only as order of magnitude estimates. Both Biltz and Roos used a method which in essence is identical with that employed in the present work. However, neither made use of the differential principle, which is so readily applicable in this instance. The heats of solution of the alloy

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(14) Thomas M. Buck, Jr., Ph.D. Dissertation, University of Pittsburgh, 1950.

(15) W. Biltz and G. Hohorst, *Z. anorg. allgem. Chem.*, **121**, 261 (1922).

(16) G. D. Roos, *ibid.*, **94**, 329 (1916).

and the two metals were determined in separate experiments and the heats of alloying were computed from those results, with no accounting being made for possible heats of mixing.

Biltz has criticized the work of Roos on the grounds that his heats of solution for the alloy and for the mixture referred to different final states. That criticism appears to be valid. As for Biltz's datum, calculations were made as if the alloy had a composition exactly 50.00%. If Biltz's alloy was of this composition, then the differences noted must be due to experimental error in both investigations, including Biltz's failure to account for heats of mixing. If, on the other hand, Biltz's alloy was of a composition nearly, but not exactly, equimolal, then that factor would enter also. An error of 0.01 in mole fraction would introduce an error of about 1800 cal./gram atom into the value reported.

In view of the known uncertainties there are probably no significant differences between the ΔH_f values determined calorimetrically and those obtained using the electrochemical cell. In three cases the calorimetric values are slightly higher, which is in the direction expected from the difference in order in the two cases. In the other case the difference is opposite to that expected. It is thus clear that the differences are too small in comparison with the uncertainties to permit an evaluation of the energies associated with the formation of magnesium–cadmium superstructures. About all that can be said is that the crude estimates based on theory appear to be high for the magnesium–cadmium system. The several theories of superstructures all indicate[17] an energy associated with the long range order of approximately $RT_c/2$, T_c being the order–disorder Curie temperature. On this basis the destruction of the several superlattices should alter the heats of formation of these alloys by roughly 300–500 cal. Differences of this magnitude should have showed up. Roos attempted to measure[16] the order–disorder transformation energy for MgCd by thermal analysis. His experiments gave a value of 140 cal./gram atom, which in view of the nature of this transformation and the method employed is probably somewhat low but may not be too far in error. The superstructures based on Mg_3Cd and $MgCd_3$ are less stable than that based on MgCd and undoubtedly have smaller energies of transformation. The magnitude of these energies makes the comparison of heats of formation a rather unattractive means for attempting their evaluation.

The failure of the heats of formation when plotted against composition to give a curve symmetrical about mole fraction 0.5 as required by the quasichemical theory has been referred to in II. There appears to be as yet no theory capable of explaining why the energy release accompanying the replacement of 25% cadmium with magnesium exceeds that of the converse process by a factor of two, or for that matter why the alloys are formed exothermally rather than endothermally. Such subleties of the alloying process appear to be for the moment solely within the province of the experimentalist.

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

PITTSBURGH, PENNA. RECEIVED JUNE 27, 1951

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA IN CHAPEL HILL]

Compounds of Zirconium and Hafnium Tetrachlorides with Esters[1,2]

BY W. S. HUMMERS, S. Y. TYREE, JR., AND S. YOLLES

Zirconium tetrachloride·2-ethyl benzoate, zirconium tetrachloride·2-methyl benzoate, zirconium tetrachloride·2-phenyl benzoate, hafnium tetrachloride·2-methyl benzoate and hafnium tetrachloride·2-ethyl benzoate have been prepared and characterized. Heats of solution of hafnium tetrachloride, zirconium tetrachloride, methyl benzoate, ethyl benzoate, phenyl benzoate and the new compounds in nitrobenzene have been determined. The heats of formation of the new compounds have been determined.

It has been shown that certain rare earth tribromides react with ethyl benzoate to evolve ethyl bromide and leave insoluble rare earth tribenzoates.[3] Differences in the rate of these reactions for individual earths has been proposed as a basis of separation. Preliminary work in this Laboratory, aimed at establishing a separation factor for zirconium and hafnium, indicated that zirconium tetrahalides react with ethyl benzoate to yield ethyl halides, but that the residue is not zirconium tetrabenzoate. Furthermore, other decomposition products were identified, indicating that the reaction is not a well-defined double decomposition of the type proposed in the rare earth work. In an effort to delineate the nature of reactions between zirconium and hafnium tetrahalides and organic esters it was decided to isolate and characterize several molecular addition compounds first, and then study their decomposition.

The present paper describes techniques for the preparation of zirconium (and hafnium) tetrachloride–ester addition compounds and reports the determination of heats of formation of the compounds.

Experimental

The Preparation of Addition Compounds.—Rosenheim and Hertzmann[4] prepared zirconium tetrachloride·2-ethyl benzoate by refluxing an ether solution of zirconium tetrachloride and ethyl benzoate. Jantsch[5] repeated the preparation. In this Laboratory, Rosenheim's preparation was repeated successfully, but the yields were very low and the

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(1) From the doctoral dissertations of W. S. Hummers and S. Yolles.

(2) Presented at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April 11, 1951.

(3) Young, Arch and Shyne, THIS JOURNAL, **63**, 957 (1941).

(4) Rosenheim and Hertzmann, *Ber.*, **40**, 812 (1907).

(5) Jantsch, *J. prakt. Chem.*, **115**, 7 (1927).