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Thermodynamic measurements in the Mg–Zn system

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ABSTRACT

New experimental values of the enthalpies of formation of intermediate phases in the Mg–Zn system at 298 K using drop-solution calorimetry in liquid tin solvent at 665 K are presented and compared with the literature data. The heat content of $MgZn_2$ is also measured at high temperature in order to deduce the evolution of the enthalpy of formation.

1. Introduction

Mg-based alloys are because of the low weight and high strength very attractive materials for transport industry. Because of low densities, they could replace in some specific cases the currently already used aluminium-based alloys provided that the mechanical properties are improved. It has been shown that among the common alloying elements, zinc increases the strength of the magnesium alloys by entailing precipitations [1]. Consequently, the optimization of the structures of Mg–Zn alloys require a precise knowledge of the thermal and chemical stabilities and of the thermodynamical functions of the phases belonging, at first, to the binary system.

The history of the thermodynamic studies on the enthalpies of formation of the phases in the Mg–Zn system can be resumed as follows:

The first measurements on $MgZn_2$ were performed by Biltz and Hohorst by acid solution calorimetry [2] and later on MgZn, $MgZn_2$ and Mg_2Zn_{11} by Schneider et al. by direct reaction calorimetry [3]. King and Kleppa determined the enthalpies of formation of the MgZn and $MgZn_2$ phases at 298 K using tin bath drop-solution calorimetry method [4]. In a more recent work, Morishita et al. determined also by acid solution calorimetry the same quantities for MgZn, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11} [5].

Based on a review of Clark et al. [6], Agarwal et al. assessed the phase equilibria by using the Calphad method [7]. From this assessment, the enthalpies of formation were calculated for the whole intermediate phases, Mg_7Zn_3, MgZn, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11}. The results are only in reasonable agreement with the experimental data of King and Kleppa [4].

Recently, Mihalkovic [8] calculated the enthalpies of formation of all the phases using the Density Functional Theory (DFT) method. They obtained values lower than those determined in the only existing assessment [7].

A discrepancy up to ±25% between the literature data is observed. Therefore it was decided to reinvestigate partly the Mg–Zn system in order to get more reliable enthalpies of formation and also heat contents which are mandatory basic thermodynamic data for the optimization of higher order Mg-based systems.

As the addition of rare earths enhances the strength of the Mg–Zn alloys [9–11], the study of the La–Mg–Zn system is of a high interest. The present work is a part of this study. The enthalpies of formation of intermediate phases in the La–Mg and La–Zn systems were previously determined by the authors [12,13]. New results on the corresponding phase diagrams were also obtained, they will be published soon and the assessment of the La–Mg–Zn phase diagram is in progress.

2. Literature data

2.1. The Mg–Zn phase diagram

As shown on Fig. 1, the assessment by the Calphad method of Agarwal et al. [7] based on the review of Clark et al. [6], is

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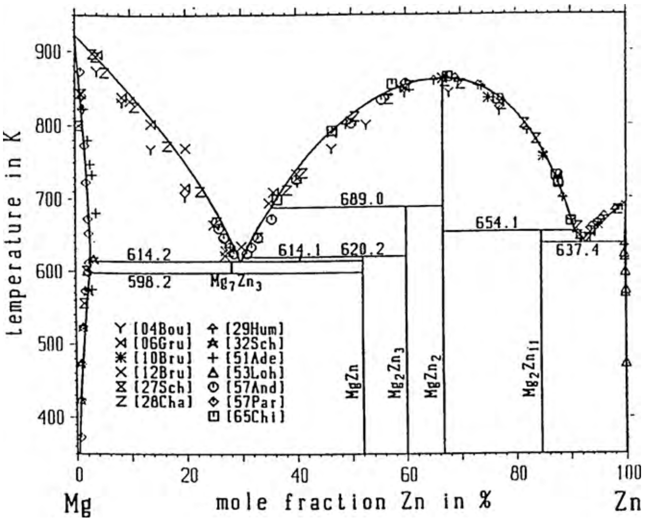

Fig. 1. The assessed Mg–Zn phase diagram from Agarwal et al. [7].

in good agreement with the experimental data concerning the temperatures of transition. Five intermetallic transition temperatures were reported: Mg_7Zn_3-peritectic decomposition at 614.2 K, MgZn-peritectic decomposition at 620.2 K, Mg_2Zn_3-peritectic decomposition at 689 K, $MgZn_2$-congruent melting at 863 K and Mg_2Zn_{11}-peritectic decomposition at 654.1 K. The solubility limit of the Mg-based solid solution is about 2.4 at.% at 600 K.

The stoichiometry of MgZn is uncertain because its composition is Zn-rich and its crystal structure is still unknown. The most reliable composition in Zn should be 51.4 at.%. However the compound will keep the designation MgZn. The stoichiometry of Mg_2Zn_3 is also uncertain [14]. A homogeneity range of about 3.1 at.%Zn has been observed around the $MgZn_2$ stoichiometric composition [15].

2.2. Enthalpy of formation of the intermediate phases

The experimental enthalpies of formation at 298 K already reported in literature are gathered in Table 1. Those calculated by DFT at 0 K are also given in this table.

Biltz and Hohorst measured the enthalpy of formation of $MgZn_2$ at 298 K by using acid solution calorimetry [2]. The samples were prepared from pure Mg (99.9%) and pure Zn (99.62%). The solvent was HCl-acid 8.8 M.

The enthalpies of formation of MgZn, $MgZn_2$ and Mg_2Zn_{11} were measured by Schneider et al. [3] by direct reaction calorimetry. Magnesium and zinc powders in stoichiometric quantities were placed into the calorimeter and the reaction of formation was performed at 643 K. The samples after reaction were checked by chemical analysis, metallographic studies and X-ray diffraction measurements.

The enthalpies of formation of $MgZn_2$ and MgZn were determined at 298 K by King and Kleppa [4]. The measurements were performed using drop-solution calorimetry in liquid tin at 773 K. The calorimeter was calibrated using the heat content of pure tungsten which does not dissolve in liquid tin at 773 K. The samples were prepared from a mixture of pure elements (Mg, 99.87% and Zn, 99.99%) weighted in stoichiometric ratios. The mixtures were melted into pyrex tubes sealed under argon atmosphere and then annealed after solidification to reach the equilibrium state. The alloys were checked by microscopic and chemical analyses. They were homogeneous and no significant changes in composition were observed with respect to the raw mixture.

More recently, new measurements of the enthalpies of formation of MgZn, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11} were performed by Morishita et al. by the acid solution calorimetric method [16–18]. Mixtures of pure elements (Mg, 99.99% and Zn, 99.99) were melted in magnesia crucibles using inductive heating. A low excess of Mg was added in compensation of Mg vapour losses. Samples of MgZn and $MgZn_2$ were annealed at 573 K in vacuum-sealed silica tubes during 72 h and 170 h, respectively. The samples were checked by X-ray diffraction analysis. They were single-phased. The samples were then dissolved in a 5 N HCl-acid solution in a Tian-Calvet calorimeter at 298 K.

From their assessment of the Mg–Zn phase diagram, Agarwal et al. [7] calculated the enthalpies of formation at 298 K of all the intermediate phases. The obtained values agree with the experimental data of King and Kleppa [4].

In a more recent work, Mihalkovic [8] calculated by the DFT method (0 K) some enthalpies of formation of intermediate compounds.

The enthalpies of DFT calculations are lower than those determined in the assessment of 1.1–3.9 kJ/mol. According to the data of heat content between 0 K and 298 K of Morishita et al. [5] the enthalpies of formation at that two temperatures do not differ more than 0.22 kJ/mol. For all the compounds an actual divergence remains. Except for the data of King and Kleppa [4], the acid solution and direct reaction calorimetry results are all much lower (up to 66%) than the data given by the assessment.

2.3. Heat contents of the intermediate phases

The heat capacities of the phases MgZn, Mg_2Zn_3, $MgZn_2$ and Mg_2Zn_{11} were measured from 2 K to 300 K using relaxation method by Morishita et al. [16–18]. Later on, the same authors measured the C_p values for these phases from 400 K to 700 K using Differential Scanning Calorimeter (DSC) [5]. Since a large crucible (Ø 20 mm × 5 mm) made from Pt was used, the heat flow was very stable and the C_p values were determined with good accuracy. The heat capacity of MgZn and Mg_2Zn_{11} were measured up to 530 K. The heat capacities of Mg_2Zn_3 and $MgZn_2$ were measured up to 640 K and 680 K, respectively. Such maximum temperatures were chosen on the basis of the melting points of the intermediate phases (see Fig. 1). The mass and metallic aspect of the samples did not change during measurements indicating that no oxidation occurred.

Table 1
Enthalpy of formation (in kJ/mol) of the compounds in the Mg–Zn system at given temperatures.

Reference	Method	ΔH_f^T (kJ/mol of atom)					T (K)
		Mg_7Zn_3	MgZn	Mg_2Zn_3	$MgZn_2$	Mg_2Zn_{11}	
[2]	Calorimetry-acid solution	–	–	–	−17.6	–	291
[3]	Direct calorimetry	–	−10.5 ± 3.1	–	−15.05 ± 1.1	−10.0 ± 2.5	298
[4]	Calorimetry-tin solution	–	−8.9 ± 0.4	–	−10.9 ± 0.4	–	298
[5]	Calorimetry-acid solution		−12.14 ± 3	−13,96 ± 3	−13.8 ± 3	−8.96 ± 3	298
[7]	Calphad calculation	−4.8	−9.6	−11.0	−11.7	−5.8	298
[8]	DFT calculation	−5.9	−13.5	–	−13.8	−7.1	0

Previous C_p values of $MgZn_2$ determined by the relaxation method from 2 K to 400 K were not consistent with the data obtained above 400 K by DSC. Therefore, C_p values of this phase were measured again in Ref. [5] from 2 K to 400 K using the relaxation method. Then for all the samples, the C_p values above 400 K obtained from DSC were connected smoothly with the data obtained from the relaxation method between 2 K and 300 K. According to the authors, the problem with $MgZn_2$ was due to an inaccurate temperature calibration of the sample stage in the first attempt.

The heat contents (H^T–H^{298}) were calculated from the C_p results for different temperatures in the range from near very low to high temperature.

3. Experimental procedure

3.1. Synthesis of the samples

In order to check the values of the enthalpies of formation determined by King and Kleppa [4] for MgZn and $MgZn_2$, four samples were synthesized. According to Drescher's work [15], three of them belong to the previously observed homogeneity range of $MgZn_2$. The zinc contents of these alloys are 65.82 at.%, 66.66 at.%, and 67.5 at.%. The fourth one corresponds to the $Mg_{66}Zn_{34}$ alloy which is constituted at room temperature by the MgZn and Mg phases in equilibrium, according to the Mg–Zn phase diagram.

Two solidification paths were used for the synthesis:

For the first three samples, a stoichiometric mixture of pure magnesium and zinc was placed into a tantalum crucible sealed under pure argon. The crucibles were heated in a resistance furnace up to 973 K which is higher than the melting point of the pure reference elements. The liquid samples were homogenized during 4 h at 973 K. The temperature was lowered down to 913 K at 20 K/h and then to 896 K by 4 K/h. The solidification occurred at about 873 K.

For the $Mg_{66}Zn_{34}$ sample, the mixture of pure Mg and Zn was placed in a tantalum crucible sealed under pure argon. The crucible was heated in a resistance furnace up to 973 K. The liquid sample was kept at this temperature for homogenization. Then the sample was quenched to room temperature and finally annealed at 550 K for 4 weeks.

3.2. Characterization of the samples

The samples were characterized by X-ray powder diffraction measurements and scanning electron microscopy (SEM).

Diffraction patterns were recorded on a Philips Expert diffractometer with a copper $K\alpha_1$ anticathode in the [10°–100°] 2θ range. The lattice parameters were determined from X-ray diffraction patterns using the PowderCell program [19] which restore a theoretical pattern from a crystal structure by means of a refinement algorithm.

SEM measurements were performed using a FEG XL30S – Oxford Instruments – microscope equipped with an energy dispersive spectrometer (EDX).

3.3. Enthalpy measurements

Calorimetric measurements were performed in a high temperature Tian-Calvet calorimeter built in the "Centre de Thermodynamique et Microcalorimétrie" (CNRS-Marseille) and extensively described in the literature [19,20]. Each of the twin cells is surrounded by a thermopile with more than 200 thermocouples. The temperature was kept at 665 ± 0.5 K for the measurements of drop-solution enthalpies and either 665 ± 0.5 K or 745 ± 0.5 K for the heat contents measurements.

3.3.1. Drop-solution enthalpies

Pieces of tin of 99.99% purity with a total mass of about 2 g were placed in a graphite crucible of 12 mm in diameter and 70 mm in height. The crucible was put at the bottom of the silica tube inserted in one of the calorimeter cells.

Just before solution experiments, the quartz tube was flushed several times with high purity argon (<2 ppm O_2). The blown volume of gas was about 15 times the volume of the airtight silica tube. A 10 cm^3/min argon flow was maintained through the cell during the whole experiment durations. Argon was in situ purified by Ti–Zr turnings placed in the hot zone of the silica tube just above the crucible. This very efficient oxygen getter acts beyond the measurement zone of the thermopile.

The Mg–Zn samples of 10–30 mg initially at room temperature were dropped through a airlock into the liquid tin bath maintained at 665 K.

At the end of each set of measurements, the calorimeter was calibrated by standard hcp-Al_2O_3 samples provided by NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA).

For each drop, the measured drop-solution effect $\Delta_{dsol}H$ represents the heat effect of the sample between the ambient temperature and the temperature of the calorimetric cell added to the solution effect at the later temperature. Within the investigated composition range, the variation of $\Delta_{dsol}H$ with solute concentration can be considered as linear within the error margin. The extrapolation to infinite dilution in order to obtain $\Delta_{dsol}H^\infty$ is then deduced. The enthalpies of formation, $\Delta_f H^{298}$ of the Mg_xZn_y compounds were obtained from the difference between the partial drop-solution enthalpies at infinite dilution of the pure Mg and Zn components and those of the compounds according to the following equation.

$$\Delta_f H^{298}(Mg_xZn_y) = x\Delta_{dsol}\overline{H}^{\infty}(Mg) + y\Delta_{dsol}\overline{H}^{\infty}(Zn) - \Delta_{dsol}\overline{H}^{\infty}(Mg_xZn_y)$$

More details on the method can be found in Ref. [12].

3.3.2. Heat content

The heat content measurements were performed using the same equipment. However, in this case, the sample initially at room temperature was dropped into the calorimeter stabilized at T. The heat content measurements were carried out on the $Mg_{.33}Zn_{.66}$ alloy from 298 K, 665 K and 745 K.

4. Results and discussion

Both X-ray diffraction and SEM measurements showed single-phased materials for the samples $Mg_{1-x}Zn_x$ (x = 65.82 at.%, 66.66 at.%, 67.5 at.%). Within the error margin for the observations it seems that the different alloys correspond to the solid solution ≪$MgZn_2$≫.

The $Mg_{66}Zn_{34}$ sample contains the MgZn phase and the solid solution centered on pure Mg. The structure parameters of the solid solution calculated using the PowderCell program [21] (a = 3.21 Å and c = 5.21 Å) are in good agreement with those reported in the JCPDS file no.35-0821 [22] for pure Mg (a = 3.209 Å and c = 5.211 Å). This result seems to confirm the very low solubility of Zn into Mg at 550 K. It will be neglected in the following.

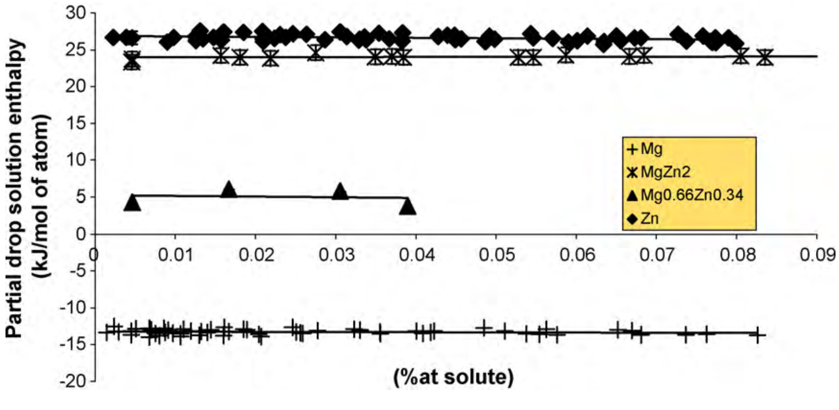

Fig. 2. Partial drop-solution enthalpies of pure Mg, pure Zn, $MgZn_2$ and $Mg_{66}Zn_{34}$ with respect to the solute concentration in molten tin.

Table 2
Partial drop-solution enthalpies at infinite dilution (solvent at $T = 665$ K) for pure Mg, pure Zn, $MgZn_2$, and $Mg_{66}Zn_{34}$. Enthalpies of formation of MgZn and $MgZn_2$ at 298 K.

	$\overline{\Delta_{dsol}H^{\infty}}$ (kJ/mol)	$\Delta_f H$ (kJ/mol)
Mg	−13.3 ± 0.7	
$Mg_{66}Zn_{34}$	5.2 ± 1.2	
MgZn		−7.9 ± 3.1
$MgZn_2$	23.9 ± 0.7	−10.4 ± 1.5
Zn	26.9 ± 0.8	

4.1. Enthalpy of formation

The linear evolutions of the partial drop-solution enthalpies of pure Mg, pure Zn, $MgZn_2$ and $Mg_{66}Zn_{34}$ versus the solute concentration in the tin bath are plotted in Fig. 2. The corresponding values are gathered in Appendix A. The three samples at 65.82 at.%Zn, 66.66 at.%Zn and 67.5 at.%Zn give identical drop-solution enthalpies within the experimental error margin. Thus, only the data of the 66.66 at.%Zn compound will be used further for the calculation of the formation enthalpy.

The partial drop-solution enthalpies at infinite dilution obtained by extrapolation to $x_{Sn} = 1$ and the enthalpies of formation of $MgZn_2$ and MgZn are reported in Table 2. Given that the solubility of Zn in solid Mg can be neglected, the enthalpy of formation of MgZn is deduced assuming that one mole of $Mg_{0.66}Zn_{0.34}$ is a combination of 0.3514 mol of pure Mg and 0.6486 mol of $Mg_{0.486}Zn_{0.514}$. The corresponding uncertainty is also twice bigger than that evaluated for $MgZn_2$.

In Fig. 3, the present results are compared to the available literature data.

The value obtained for $MgZn_2$ is in good agreement with that reported by King and Kleppa [4]. The difference between these two values is 0.5 kJ/mol only. Taking into account the experimental uncertainties, an agreement is also observed between the present values and the Agarwal et al.'s assessment data for MgZn and $MgZn_2$ [7]. This result supports the reliability of the data of the Calphad assessment of Agarwal et al. which are also in good agreement with the data of King and Kleppa. It can reasonably be assumed that this agreement would occur for the other intermediate phases.

The large uncertainty reported by Morishita et al. [5] depends on the measurements. In fact, the enthalpies of dissolution of metals into acid solutions are several ten times higher than those obtained into metallic solvent. As a consequence, the enthalpy of formation of metals cannot be determined with a good accuracy by this method.

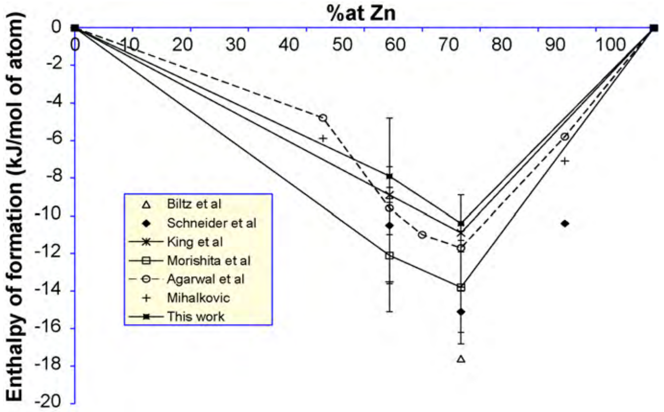

Fig. 3. Enthalpies of formation of the Mg–Zn phases. Comparison between present results and literature data.

Table 3
Heat content of $MgZn_2$ (kJ/mol).

Temperature (K)	H^T-H^{298} (kJ/mol of atom)
665	9.8 ± 0.6
745	11.8 ± 0.6

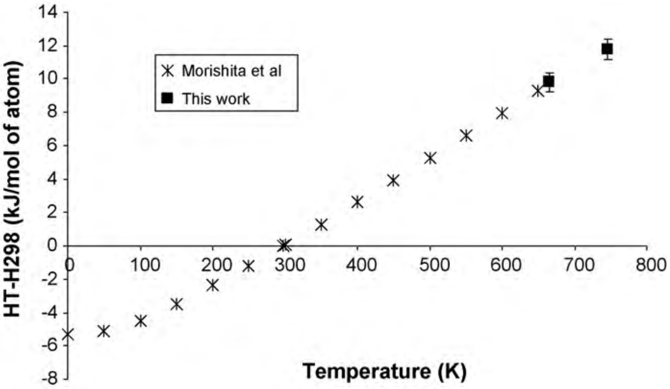

Fig. 4. Heat content of $MgZn_2$ versus temperature.

4.2. Heat content of $MgZn_2$

The heat content of $MgZn_2$ was measured from 298 K to respectively 665 K and 745 K. Several samples were used for each temperature. The results are reported in Appendix B and the average values are given in Table 3.

In Fig. 4, the results are compared to the calculated heat contents deduced by integration of the heat capacities [5]. The results obtained from different experimental methods are in very good agreement.

The variation of the enthalpy of formation can then be calculated. For example from 298 K to 665 K the difference is 22 J. This value falls into the error margin and the enthalpy of formation can be considered as constant all along the temperature interval.

5. Conclusions

New measurements of enthalpies of formation of intermediate phases in the Mg–Zn system were performed using drop-solution calorimetry in tin solvent at 665 K. The values are in good agreement with the literature data of [4]. Since they are in concordance with the assessed ones [7], we can assume that the values assessed by Agarwal et al. for the Mg–Zn system are reliable. Then they can be used for higher order assessment, in particular for the La–Mg–Zn system. Moreover the low solubility of Zn in solid Mg has been confirmed and new arguments have been given for the existence of a phase width for $MgZn_2$.

Acknowledgment

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Appendix A. Partial mixing enthalpy of alloys and pure elements of the Mg–Zn system in liquid tin at 665 K. These values are referred to the reference state of Mg and Zn at 298 K and to the liquid tin at 665 K

Zn			Zn			Magnesium			Magnesium		
X	ΔH_m	$\Delta\,(\Delta H_m)$	X	ΔH_m	$\Delta\,(\Delta H_m)$	X	ΔH_m	$\Delta\,(\Delta H_m)$	X	ΔH_m	$\Delta\,(\Delta H_m)$
0.0160	27.4	0.00	0.0231	27.1	0.00	0.0161	−12.7	0.04	0.0355	−13.3	0.20
0.0264	27.1	0.05	0.0354	27.2	0.09	0.0015	−13.4	0.54	0.0423	−13.2	0.26
0.0383	27.3	0.00	0.0492	26.9	0.00	0.0030	−13.3	0.26	0.0485	−12.7	0.22
0.0543	27.2	0.00	0.0651	26.8	0.01	0.0070	−12.9	0.92	0.0563	−12.9	0.09
0.0727	27.1	0.01	0.0772	26.5	0.04	0.0097	−13.4	0.25	0.0097	−13.5	0.17
0.0090	26.0	0.12	0.0157	26.3	0.00	0.0130	−13.7	0.09	0.0277	−13.1	0.07
0.0210	26.1	0.04	0.0286	26.3	0.02	0.0167	−13.2	0.50	0.0418	−13.4	0.15
0.0329	26.3	0.01	0.0383	26.2	0.00	0.0068	−14.0	0.12	0.0538	−13.5	0.18
0.0449	26.3	0.04	0.0486	26.1	0.00	0.0207	−13.9	0.44	0.0652	−13.0	0.22
0.0601	26.2	0.04	0.0634	25.7	0.06	0.0356	−13.6	0.08	0.0737	−13.7	0.41
0.0774	26.0	0.00	0.0799	25.8	0.00	0.0511	−13.2	0.64	$MgZn_2$		
0.0134	26.5	0.01	0.0046	26.6	0.13	0.0681	−13.7	1.11	X	$\Delta_m H$	$\Delta\,(\Delta_m H)$
0.0238	26.7	0.02	0.0147	26.7	0.06	0.0826	−13.7	0.25	0.0218	23.9	0.12
0.0367	26.5	0.00	0.0247	27.2	0.10	0.0045	−13.7	0.35	0.0370	24.1	0.12
0.0498	26.4	0.00	0.0336	26.7	0.00	0.0080	−13.8	0.40	0.0528	24.0	0.25
0.0635	26.1	0.02	0.0448	27.0	0.07	0.0119	−13.2	0.12	0.0666	24.1	0.37
0.0768	26.2	0.00	0.0571	26.5	0.01	0.0161	−13.8	0.22	0.0806	24.2	0.14
0.0022	26.7	0.00	0.0681	26.6	0.00	0.0204	−13.6	0.21	0.0045	23.4	0.02
0.0098	26.7	0.01	0.0774	26.6	0.01	0.0256	−13.4	0.41	0.0157	24.2	0.18
0.0209	26.5	0.00	0.0038	26.7	0.03	0.0051	−12.9	0.12	0.0275	24.6	0.18
0.0330	26.4	0.00	0.0126	26.2	0.06	0.0091	−13.0	0.11	0.0384	24.0	0.02
0.0457	26.5	0.02	0.0224	26.5	0.01	0.0132	−13.2	0.19	0.0547	24.0	0.00
0.0590	26.0	0.05	0.0338	26.4	0.00	0.0185	−12.9	0.30	0.0685	24.2	0.14
0.0737	26.1	0.00	0.0487	26.1	0.02	0.0251	−13.3	0.41	0.0046	23.7	0.37
0.0185	27.4	0.12	0.0655	26.2	0.02	0.0323	−12.9	0.47	0.0180	23.9	0.33
0.0314	26.8	0.01	0.0770	26.0	0.00	0.0401	−13.2	0.14	0.0350	24.0	0.14
0.0428	26.8	0.00	*Magnesium*			0.0140	−13.4	0.18	0.0587	24.3	0.03
0.0547	26.6	0.02	X	$\Delta_m H$	$\Delta\,(\Delta_m H)$	0.0330	−13.0	0.14	0.0835	24.0	−0.01
0.0673	26.6	0.01	0.0024	−12.5	0.41	0.0554	−13.6	0.13	0.1000	23.6	−0.02
0.0790	26.6	0.00	0.0068	−12.8	0.48	0.0669	−13.1	0.21	$Mg_{66}Zn_{34}$		
0.0131	27.6	0.03	0.0086	−12.8	0.59	0.0763	−13.6	0.44	0.0046	4.3	0.09
0.0209	27.5	0.03	0.0110	−12.9	0.24	0.0107	−13.5	0.12	0.0167	6.1	0.09
0.0305	27.4	0.02	0.0144	−13.0	0.35	0.0259	−13.5	−0.16	0.0306	5.8	0.09
0.0439	27.0	0.04	0.0189	−13.0	0.20	0.0409	−13.5	−0.22	0.0390	3.8	0.25
0.0614	26.8	0.05	0.0045	−13.2	0.53	0.0576	−13.7	−0.31			
0.0758	26.9	0.01	0.0075	−13.5	0.19	0.0087	−13.3	0.13			
0.0125	26.8	0.10	0.0106	−13.9	0.15	0.0246	−12.6	0.19			

Appendix B. Heat contents H^T–H^{298} (kJ/mol) of $MgZn_2$ (T = 665 K and 745 K)

T = 665 K			T = 745 K		
m (mg)	H^T–H^{298}	$\Delta\,(H^T$–$H^{298})$	m (mg)	H^T–H^{298}	$\Delta\,(H^T$–$H^{298})$
7.75	9.24	0.04	25.84	11.39	0.16
9.96	10.08	0.16	9.98	11.55	0.21
21.69	9.65	0.02	27.35	11.69	0.08
29.85	9.83	0.00	19.53	12.18	0.13
34.66	9.52	0.00	34.63	12.05	0.09
35.02	9.40	0.00	12.91	11.76	0.56
11.33	10.24	0.23	29.14	12.00	0.19
19.65	10.02	0.12			
25.87	10.06	0.14			
27.50	9.68	0.07			
29.11	9.76	0.15			
12.96	9.94	0.14			

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