



Calorimetric study of the enthalpy of mixing in the liquid systems Li-Zn and Li-Sn-Zn

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ABSTRACT

Partial and integral molar enthalpies of mixing of binary liquid Li-Zn alloys and ternary liquid Li-Sn-Zn alloys were determined by drop calorimetry at 823 K. The binary system was investigated up to $x_{Zn} = 0.85$ and the integral mixing enthalpy was described with a Redlich-Kister-polynomial. Li-Zn shows an exothermic behavior and a minimum molar mixing enthalpy of about $\Delta H_{mix} = -11.7 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{Zn} = 0.6$. The mixing enthalpy along nine ternary sections of Li-Sn-Zn (A: $x_{Li}/x_{Sn} \approx 9:1$, B: $x_{Li}/x_{Sn} \approx 1:4$, C: $x_{Sn}/x_{Zn} \approx 9:1$, D: $x_{Sn}/x_{Zn} \approx 7:3$, E: $x_{Sn}/x_{Zn} \approx 1:1$, F: $x_{Li}/x_{Zn} \approx 1:3$, G: $x_{Li}/x_{Zn} \approx 1:1$, H: $x_{Li}/x_{Zn} \approx 3:2$, I: $x_{Li}/x_{Zn} \approx 7:3$) was investigated. Solid pieces of Li, Sn, and Zn respectively were dropped to the liquid binary starting alloys in the calorimeter at 823 K. The integral values at the crossing points of the various sections show excellent agreement. The course of the partial and integral enthalpy values along the sections A, D, E, F, G, H, and I indicate multiple-phase regions. The occurrence of such partially liquid and de-mixed liquid regions is discussed and compared with a calculated version of the isothermal section at 823 K which exhibits a large ternary liquid miscibility gap. The experimental ternary data allocated to the fully liquid monophasic regions was numerically fitted based on a Redlich-Kister-Muggianu polynomial for substitutional solutions including ternary interactions. In addition, a comparison with enthalpy values from the extrapolation methods based on binary data according to the Muggianu and Toop model, respectively, is shown. Both models fail to accurately reproduce the experimental values. Iso-enthalpy plots of calculated integral mixing enthalpy for stable and metastable fully homogeneous liquid alloys for the entire ternary system are shown.

1. Introduction

Due to the ever-increasing demand for more efficient energy storage, there is an enormous need for improvements in the individual components of common electricity storage systems such as Li-ion batteries. Conventional graphite-based anodes for Li-ion batteries are abundant and persistent, but suffer from low specific capacities (e.g., $372 \text{ mAh}\cdot\text{g}^{-1}$ for graphite). Alternatives, among others, are intermetallic formation anodes, e.g., based on Sn. Tin has a comparable high theoretical capacity of $994 \text{ mAh}\cdot\text{g}^{-1}$. Pure Sn electrodes, however, feature large volume changes during lithiation and de-lithiation leading to crack formation and degradation what results in poor cycling performance [1,2].

One possible way to overcome this problem, among other options, is making use of a so-called “self-healing effect”. Such an effect can be based on various mechanisms, one is the development of a liquid phase which fills the formed cracks and allows fast diffusion what also

facilitates the elimination of concentration gradients. For that, metallic anode materials are alloyed with low melting metals to bring the electrodes in a partially liquid state and initiate the effect. The added metal should be also active on lithiation to avoid a larger loss in specific capacity. The feasibility was demonstrated, for example, on the basis of the Ga-Sn system [3] and the Ga-In-Sn system [4].

Nevertheless, due to the relatively high price of Ga and In, alternative systems with lower-cost metals, e.g., Zn, are needed. Sn and Zn as anode materials for Li-ion batteries were investigated by several groups, e.g., Zhang et al. for Sn [5] and Hwa et al. [6] and Singh et al. for Zn [7]. Due to the formation of intermetallic compounds, both elements are active towards Li. The theoretical capacity of Sn lithiated up to $\text{Li}_{4.25}\text{Sn}$ is $987 \text{ mAh}\cdot\text{g}^{-1}$, in the case of Zn lithiated up to LiZn it is about $410 \text{ mAh}\cdot\text{g}^{-1}$. In order to understand the lithiation mechanism of Sn-Zn alloys, it is necessary to have a full structural and thermodynamic description of the ternary system Li-Sn-Zn. The systems Li-Zn and Li-Sn-

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Zn are currently being investigated in terms of experimental phase diagram assessments by our group with respect to crystal structures and phase equilibria. Information about the system at battery operating temperatures (263–328 K) can be obtained only by CALPHAD calculations based on high temperature data extrapolation to lower temperature regimes. Experimental thermochemical data, in particular heat capacities, formation enthalpies, and mixing enthalpies are still indispensable for reliable thermodynamic assessments. In this work, the enthalpies of mixing of the liquid systems Li-Zn and Li-Sn-Zn at 823 K are determined by means of drop calorimetry.

2. Literature review

For the constituent binary systems, this literature review focuses only on publications concerning thermochemical quantities, but not on published phase diagram descriptions or crystal structures.

2.1. Li-Sn

Kubaschewski et al. determined enthalpies of formation of Li-Sn phases already in 1938 [8]. In 1981, Wen et al. conducted a thermodynamic study in the binary Li-Sn in the temperature range from 633 to 863 K performing coulometric titrations and electromotive force (EMF) measurements [9]. Moser et al. determined mixing enthalpies of the liquid system by high temperature calorimetry for the composition range $x_{\text{Li}} = 0.01$ to 0.5 and $x_{\text{Li}} = 0.87$ to 0.99 in 1986 [10]. The same group performed EMF measurements in the temperature range between 777 and 975 K in 1999 [11]. The enthalpies of dissolution of Li in liquid Sn were published by Yassin et al. in 2001 [12]. In 2013, Fürtauer et al. determined partial and integral molar enthalpies of mixing in the liquid system at 1073 K over the whole composition range as well as at 773 K from $x_{\text{Li}} = 0.0$ to 0.63 and $x_{\text{Li}} = 0.92$ to 1.0. The mixing of Li and Sn is described as purely exothermic and has an integral enthalpy minimum of about $\Delta H_{\text{mix}} = -37000 \text{ J}\cdot\text{mol}^{-1}$ at $x_{\text{Sn}} = 0.2$ at 1073 K [13]. Based on these data Li et al. published a comprehensive thermodynamic assessment of the system and discussed the appearance of a “Li₄Sn” associate in the liquid phase [14].

2.2. Li-Zn

Smith and Moser did a review of the thermodynamic properties of binary lithium systems including Li-Zn in 1976 [15]. Hoshino et al. conducted electrochemical studies (EMF) of the liquid system using liquid salt electrolyte (LiCl/KCl eutectics) at 773 K in 1973 [16]. In 1989, Moser et al. investigated enthalpies of mixing of the liquid system Li-Zn at 820 K using reaction calorimetry [17]. In 1993, the activity of Li was determined in terms of EMF studies from Gasior and Moser [18]. In 2016, Debski et al. determined enthalpies of mixing by means of drop calorimetry at 814 K. The minimum of the generally exothermic integral enthalpy of mixing was observed to be at $x_{\text{Zn}} = 0.62$ and $\Delta H_{\text{mix}} = -12300 \text{ J}\cdot\text{mol}^{-1}$. In addition, they measured the formation enthalpies for the intermetallic phases HT-Li₂Zn₃, HT-Li₂Zn₅ and HT-LiZn₄ [19]. The same group published standard formation enthalpies of LiZn, Li₂Zn₃, LiZn₂, Li₂Zn₅ and LiZn₄ in terms of solution calorimetry [20].

2.3. Sn-Zn

Literature generally reports positive values for the enthalpy of mixing in the liquid system Sn-Zn over the whole composition range. Kleppa determined the heats of mixing in the system Sn-Zn at 703 K and 798 K [21,22]. Schürmann et al. investigated enthalpies of mixing at different temperatures in 1961 [23]. Lee published a thermodynamic assessment of the Sn-Zn system in 1996 [24]. In general, the interactions of liquid Sn and Zn are described as very weak and show a maximum at approx. $\Delta H_{\text{mix}} = 3000 \text{ J}\cdot\text{mol}^{-1}$ at about $x_{\text{Zn}} = 0.6$.

2.4. Li-Sn-Zn

At present, the authors are not aware of any publications on the enthalpy of mixing in the ternary system Li-Sn-Zn. A thermodynamic assessment including calculated isothermal sections of the Li-Sn-Zn phase diagram at different temperatures was published by Turchi et al. in 2014 [25], however, no ternary data were considered.

So far, two ternary phases have been identified in terms of their crystal structure, namely Li₂SnZn by Schuster in 1966 [26], by Pobitschka and Schuster in 1978 [27], respectively, and Li₃Sn₄Zn₂ by Stegmaier and Fässler in 2013 [28].

3. Experimental

All the measurements, both in the binary Li-Zn system and in the ternary Li-Sn-Zn system, were carried out at 823 K. Samples were made from pure elements: Li rods (Sigma-Aldrich, diam. 12.7 mm, 99.9 % trace metals basis), Sn rods (Alfa Aesar, 99.9985 %) for drops, Sn shots (smart elements, 1–3 mm, 99.999 %) for the starting alloys and Zn shots (Alfa Aesar, 1–5 mm, 99.999 % metals basis). The latter was cleaned by filtration of the liquid metal in quartz glass through quartz glass wool, in an overpressure of Ar of about 0.5 bar to remove the surface oxide layer. Lithium surface impurities were mechanically removed by scraping before sample preparation. To avoid surface reactions of Li with ambient air sample preparation was done in an Ar-filled glove box (MBraun Ar 5.0, O₂ ≤ 0.1 ppm, H₂O ≤ 0.6 ppm). The general experimental procedure is similar to former investigations of ternary, lithium-containing, intermetallic systems which were done in our group, e.g., Cu-Li-Sn [13], Li-Sb-Sn [29] and Ga-Li-Sn [30]. The measuring device used was an isoperibolic Calvet twin micro-calorimeter HT-1000 (Setaram, France) with two 3D type-S thermopiles (approx. 230 junctions each) for heat flow detection, Pt-100 thermo-resistors for sample temperature measurement and type S thermocouples for furnace control. Temperature differences down to 10⁻⁴ K between the two cells are detectable. A detailed description of the measurement procedure, the programming of the LabView program and the evaluation was given by Flandorfer et al. [31]. Data evaluation and integration was done with OriginLab.

By means of an automatic insertion system, 30 drops were performed per measurement, whereby 5 drops were used for calibration. The calorimeter system was evacuated (to the low 10⁻² mbar range) and flushed with Ar three times. Measurements were performed in a dynamic Ar flow (purity $x_{\text{Ar}} = 0.99999$; purified from oxygen with an Agilent Gas Clean Filter) of 50 ml·min⁻¹. Before the first drop, the measuring system was equilibrated for about 20 h until the baseline was stable. Pieces of Ti-sheet placed underneath the crucible were used as oxygen getter material during the measurements. The time frame between two drops was 2400 s (except 3600 s for sections D and E; this was necessary to make sure that the reaction was completed before the next drop) using a data acquisition interval of 0.5 s for the heat flow.

Fe crucibles (70 mm length, 12 mm inner diameter) were used for measurements starting from pure Li. They were cleaned with ethanol and acetone and dried prior the experiment. It was not possible to start from pure Zn due to the high vapor pressure and resulting massive evaporation. Since Fe and Zn form intermetallic phases, Fe crucibles were not suitable for measurements going up to higher (>50 at. % Zn) Zn contents. Therefore, BN crucibles (length 70 mm, inner diameter 11 mm) were used starting from a mixture of 50 at. % Zn and 50 at. % Li to measure to higher Zn contents. In order to remove boric acid from the surface, the BN crucibles were stored in methanol for 48 h, afterwards they were treated with a heating program (150 °C for 600 min, 450 °C for 120 min, 900 °C for 60 min) in dynamic vacuum to eliminate methyl ester. BN crucibles were used for all measurements in the ternary system.

Experiments were performed along sections starting from the constituent binaries Li-Sn, Li-Zn and Sn-Zn. The starting concentrations were Li₄₅Sn₅₅ (A), Li₂₀Sn₈₀ (B), Sn₉₀Zn₁₀ (C), Sn₇₀Zn₃₀ (D), Sn₅₀Zn₅₀ (E),

$\text{Li}_{25}\text{Zn}_{75}$ (F), $\text{Li}_{50}\text{Zn}_{50}$ (G), $\text{Li}_{60}\text{Zn}_{40}$ (H) and $\text{Li}_{70}\text{Zn}_{30}$ (I). All sections are illustrated in Fig. 1.

For measurements in the Li-Zn system starting from pure Li the calibration was done with 5 drops of Li metal at the beginning of each measurement. For all other measurements, five pieces of NIST (National Institute of Standards and Technology) SRM 720 standard sapphire (approx. 30 – 100 mg each) were dropped at the end of each measurement.

The calorimeter constant k was determined using following equation:

$$k = \frac{\Delta_{T_d \rightarrow T_c} H_{\text{ref}} \cdot n_{\text{ref}}}{S^{T_d \rightarrow T_c}} \quad (1)$$

The theoretical enthalpy value H_{ref} in case of Li as a calibration substance was calculated from the SGTE (Scientific Group Thermodata Europe) unary database, so-called Dinsdale polynomials [32], and from polynomials provided from the NIST (National Institute of Standards and Technology) in the case of sapphire calibration. The molar amount of the reference material is represented by n_{ref} , the drop temperature by T_d , the calorimeter temperature by T_c and the integrated voltage signal from the thermopiles by S (in μVs).

The enthalpy values for each sample drop were calculated by multiplication of the calorimeter constant with the respective integrated signal:

$$\Delta H_S = S^{T_d \rightarrow T_c} \cdot k \quad (2)$$

The molar enthalpy of mixing for each drop was then calculated according to following relation:

$$\Delta_{\text{mix}} H_i = \frac{\Delta H_S - \Delta_{T_d \rightarrow T_c} H_i \cdot n_i}{n_i} \quad (3)$$

n_i represents the molar amount of the dropped element while the enthalpy increment ΔH_i needed to heat the dropped element from T_d to

T_c and to melt it is calculated from the SGTE unary data base [32]. If the molar amount of the starting material in the crucible is large and the one of the drops comparably small $\Delta_{\text{mix}} H_i$ can be considered to correspond to the partial enthalpy of mixing, $\Delta_{\text{mix}} \bar{H}_i$, of the component dropped.

The integral molar enthalpy of mixing is given by:

$$\Delta_{\text{mix}} H_m = \frac{n_{\text{start}} \cdot \Delta_{\text{mix}} H_{\text{start}} + \sum n_i \cdot \Delta_{\text{mix}} H_i}{n_{\text{start}} + \sum n_i} \quad (4)$$

Where n_{start} defines the total molar amounts of elements in the crucible prior the first drop and $\Delta_{\text{mix}} H_{\text{start}}$ is the integral molar enthalpy of mixing of the starting alloy. The integral enthalpies of mixing for the starting alloys for Li-Zn were calculated based on the interaction parameters resulted from the experiments in this study. In the case of Li-Sn, the calculation was based on data from Fürtauer et al. [13], for the binary Sn-Zn alloys on data given by Lee et al. [24]; see Table 1.

Errors were determined by means of error propagation calculation. The errors of peak integrations of respective effects were estimated, standard deviations of the calibration constants were determined for every experiment, while weighing errors were shown to be negligible and therefore not considered. For measurements in the ternary system, the errors of the initial starting values of the respective binary systems

Table 1

Binary interaction parameters in the systems Li-Zn, Li-Sn and Sn-Zn and ternary interaction parameters in the system Li-Sn-Zn.

System	Reference	${}^0\text{L} / {}^0\text{M}$ [J·mol ⁻¹]	${}^1\text{L} / {}^1\text{M}$ [J·mol ⁻¹]	${}^2\text{L} / {}^2\text{M}$ [J·mol ⁻¹]
Li-Zn	Own data fit	-43996 ± 105	21722 ± 250	4407 ± 560
Li-Sn	[13]	-111137	-124601	-89726
Sn-Zn	[24]	12728	-5074	
Li-Sn-Zn	Own data fit	-324767 ± 22830	81227 ± 11740	-13790 ± 10370

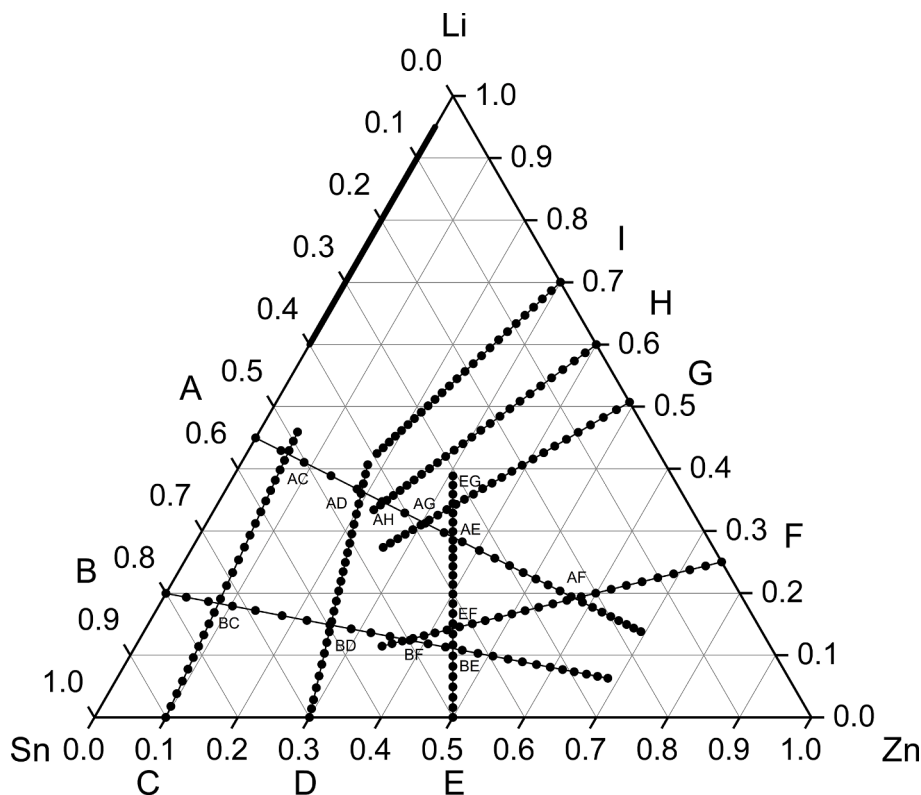


Fig. 1. Investigated sections in the system Li-Sn-Zn at 823 K with labelled intersection points. Thick line indicates the solid or semi-liquid concentrations in the binary system Li-Sn.

were included.

For the binary system Li-Zn, errors of partial and integral molar values are generally within a few hundreds of $\text{J}\cdot\text{mol}^{-1}$. For the addition of Zn to Li-Sn alloys (sections A-B) the maximum error for partial enthalpy values was less than $1500\text{ J}\cdot\text{mol}^{-1}$, this of the integral enthalpy max less than $450\text{ J}\cdot\text{mol}^{-1}$. For the addition of Li to Sn-Zn alloys (sections C-E) the maximum error for partial enthalpy values was less than $1700\text{ J}\cdot\text{mol}^{-1}$, this of the integral enthalpy max less than $650\text{ J}\cdot\text{mol}^{-1}$. For the addition of Sn to Li-Zn alloys (sections F-I) the maximum error for partial enthalpy values was less than $2000\text{ J}\cdot\text{mol}^{-1}$, this of the integral enthalpy max less than $700\text{ J}\cdot\text{mol}^{-1}$.

Thermal analysis was carried out in a Netzsch DSC 404 F1. The device was evacuated and flushed with Ar three times before heating and an Ar-flow of $20\text{ ml}\cdot\text{min}^{-1}$ was established. The measurements were carried out in Ta crucibles put on flat alumina discs. Temperature calibration was done with In, Sn, Ag and Au. The heating respectively cooling rate was $5\text{ K}\cdot\text{min}^{-1}$ and the maximum temperature was 973 K .

Powder XRD was performed on a Bruker D8 diffractometer with Bragg-Brentano pseudo-focusing geometry, $\text{CuK}\alpha$ radiation (40 kV , 40 mA with Ni filter) and a LynxEye detector.

4. Results and discussion

4.1. The binary system Li-Zn

Measurements in the binary system Li-Zn were performed at 823 K . They were started either from pure lithium or from a binary mixture. Starting from pure Zn was not possible due to significant evaporation because of the high vapor pressure of Zn at that temperature. When starting with pure lithium, an iron crucible was used, while a BN crucible was used for the binary mixtures. Proceeding like that it was possible to measure from pure lithium up to a zinc content of $x_{\text{Zn}} = 0.85$. The measured values for partial and integral molar enthalpies of mixing are shown in Table S1 in the supplementary material.

The enthalpies of mixing were extrapolated to pure Zn with a common Redlich-Kister fit [33] using equation (5):

$$\Delta_{\text{mix}}H_{ij} = x_i x_j \sum_{\nu=0}^{\nu} {}^{\nu}L_{ij} \cdot (x_i - x_j)^{\nu} \quad (5)$$

The indices i and j correspond to the elements Li and Zn, whereas L are the binary interaction parameters. ν represents the order of the interaction parameters. The evaluated binary interaction parameters are shown in Table 1. A satisfactory fit could be achieved with only two parameters. The data plot and Redlich-Kister fit of the enthalpy of

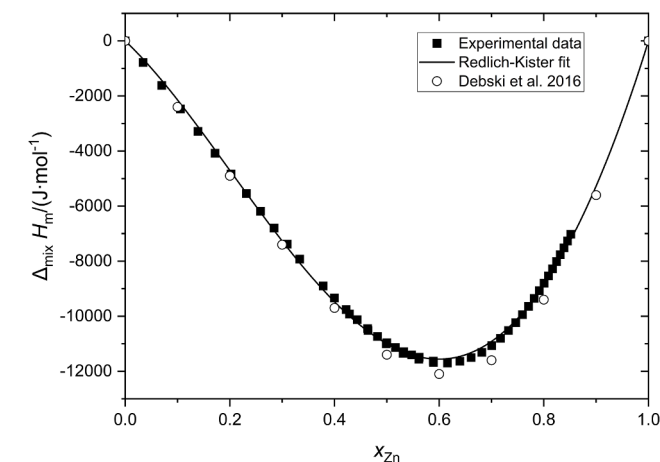


Fig. 2. Experimental integral molar enthalpies of mixing of liquid Li-Zn alloys at 823 K . Solid line shows the Redlich-Kister fit and extrapolation to pure Zn. Measurements from Debski et al. were performed at 814 K [19].

mixing of liquid Li-Zn alloys at 823 K is illustrated in Fig. 2. The values are in good agreement with those from recent literature reports which were measured at 814 K [19]. The integral molar enthalpy of mixing is exothermic over the whole composition range and the minimum value is found to occur at approx. $x_{\text{Zn}} = 0.6$ in both works. The enthalpy values at this point differ by about $400\text{ J}\cdot\text{mol}^{-1}$ only; $-11700 \pm 200\text{ J}\cdot\text{mol}^{-1}$ in our work compared to the literature value of $-12100 \pm 700\text{ J}\cdot\text{mol}^{-1}$ in [19]. Regarding the errors of the methods applied this is excellent agreement.

The limiting partial molar enthalpy of Zn in liquid Li at 823 K was determined by dropping small pieces of Zn into a Li bath up to $x_{\text{Zn}} = 0.04$. The partial molar enthalpies of mixing were extrapolated to pure Li via linear regression resulting in $\Delta_{\text{mix}}\bar{H}_i^{\infty} = -21800 \pm 245\text{ J}\cdot\text{mol}^{-1}$. This extrapolation is illustrated in Figure S1 in the supplementary material.

4.2. The ternary system Li-Sn-Zn

Nine different sections in the ternary system Li-Sn-Zn were investigated at 823 K . Lithium was dropped into liquid mixtures with molar concentration ratios of $x_{\text{Sn}}/x_{\text{Zn}} \approx 9:1$, $x_{\text{Sn}}/x_{\text{Zn}} \approx 7:3$, $x_{\text{Sn}}/x_{\text{Zn}} \approx 1:1$, tin was dropped into $x_{\text{Li}}/x_{\text{Zn}} \approx 1:3$, $x_{\text{Li}}/x_{\text{Zn}} \approx 1:1$, $x_{\text{Li}}/x_{\text{Zn}} \approx 3:2$, $x_{\text{Li}}/x_{\text{Zn}} \approx 7:3$ and zinc was dropped into $x_{\text{Li}}/x_{\text{Sn}} \approx 9:11$, $x_{\text{Li}}/x_{\text{Sn}} \approx 1:4$. This is illustrated in Fig. 1. Integral molar enthalpies of mixing for the different sections at their intersection points are given in Table 2. Deviations are in the range of about $0 - 2000\text{ J}\cdot\text{mol}^{-1}$ and prove therefore excellent agreement of different sections. The measured values for partial and integral molar enthalpies of mixing are shown in Tables S2-S4 in the supplementary material.

The integral enthalpies of mixing in the entire system were described using a least square fit according to a Redlich-Kister-Muggianu polynomial [34], subsequently referred to as Muggianu polynomial. Only values from the fully liquid single-phase regions were considered for these calculations.

$$\begin{aligned} \Delta_{\text{mix}}H_{ijk}^{\text{RKM}} = & x_i x_j \sum_{\nu} {}^{\nu}L_{ij} \cdot (x_i - x_j)^{\nu} + x_j x_k \sum_{\nu} {}^{\nu}L_{jk} \cdot (x_j x_k)^{\nu} \\ & + x_k x_i \sum_{\nu} L_{ki} \cdot (x_k - x_i)^{\nu} + x_i x_j x_k \cdot ({}^0M_{ijk} \cdot x_i + {}^1M_{ijk} \cdot x_j \\ & + {}^2M_{ijk} \cdot x_k) \end{aligned} \quad (6)$$

The variables i , j and k are lithium, tin, and zinc, respectively. While the variable L stands for the binary interaction parameters (ν represents the order), M represent the ternary interaction parameters. All interaction parameters are given in Table 1.

The Muggianu polynomial [34] is based on the extrapolation of constituent binary enthalpy values into the ternary system according to Muggianu and added ternary interaction represented by the M -parameters. The M -parameters were evaluated by the least square fit of our experimental ternary data. When the enthalpy values are calculated without the ternary interaction, they correspond to the Muggianu extrapolation model. A further model to describe the integral molar enthalpy of mixing via extrapolation is the use of the Toop model [35]. Contrary to the Muggianu model, which is symmetric, the Toop model is asymmetric. That means there are two similar and one divergent binary system. In our case, the divergent system is Sn-Zn since it is slightly endothermic and regular while the other two systems are strongly exothermic, and the minima are shifted to the Li-rich region in Li-Sn and the Zn-rich region in Li-Zn.

$$\begin{aligned} \Delta_{\text{mix}}H_{ijk}^{\text{Toop}} = & \frac{x_j}{1-x_i} \Delta_{\text{mix}}H_{ij}(x_i, 1-x_i) + \frac{x_k}{1-x_i} \Delta_{\text{mix}}H_{ik}(x_i, 1-x_i) \\ & + (x_j + x_k)^2 \Delta_{\text{mix}}H_{jk} \left(\frac{x_j}{x_j + x_k}, \frac{x_k}{x_j + x_k} \right) \end{aligned} \quad (7)$$

The variables i , j and k are lithium, tin, and zinc, respectively and thus his formulation describes Sn-Zn as the divergent sub-system. The calculated values along each section are plotted in comparison to the experimental data points in Fig. 3 (measurement series A and B), Fig. 4

Table 2Experimental integral molar enthalpies of mixing in $\text{J}\cdot\text{mol}^{-1}$ at respective intersection points at 823 K (see Fig. 1).

	A	B	C	D	E	F	G	H
Intersection	$\text{Li}_{45}\text{Sn}_{55} + \text{Zn}$	$\text{Li}_{20}\text{Sn}_{80} + \text{Zn}$	$\text{Sn}_{90}\text{Zn}_{10} + \text{Li}$	$\text{Sn}_{70}\text{Zn}_{30} + \text{Li}$	$\text{Sn}_{50}\text{Zn}_{50} + \text{Li}$	$\text{Li}_{25}\text{Zn}_{75} + \text{Sn}$	$\text{Li}_{50}\text{Zn}_{50} + \text{Sn}$	$\text{Li}_{60}\text{Zn}_{40} + \text{Sn}$
AC	-23000		-23900					
AD	-20100			-19000				
AH	-19700							-20600
AG	-18100						-18700	
AE	-17600				-16700			
AF	-9500					-9400		
BC		-9400	-9500					
BD		-6500		-6300				
BF		-4500				-5200		
BE		-3600						
EF					-3900	-6100		
EG					-23400		-21800	

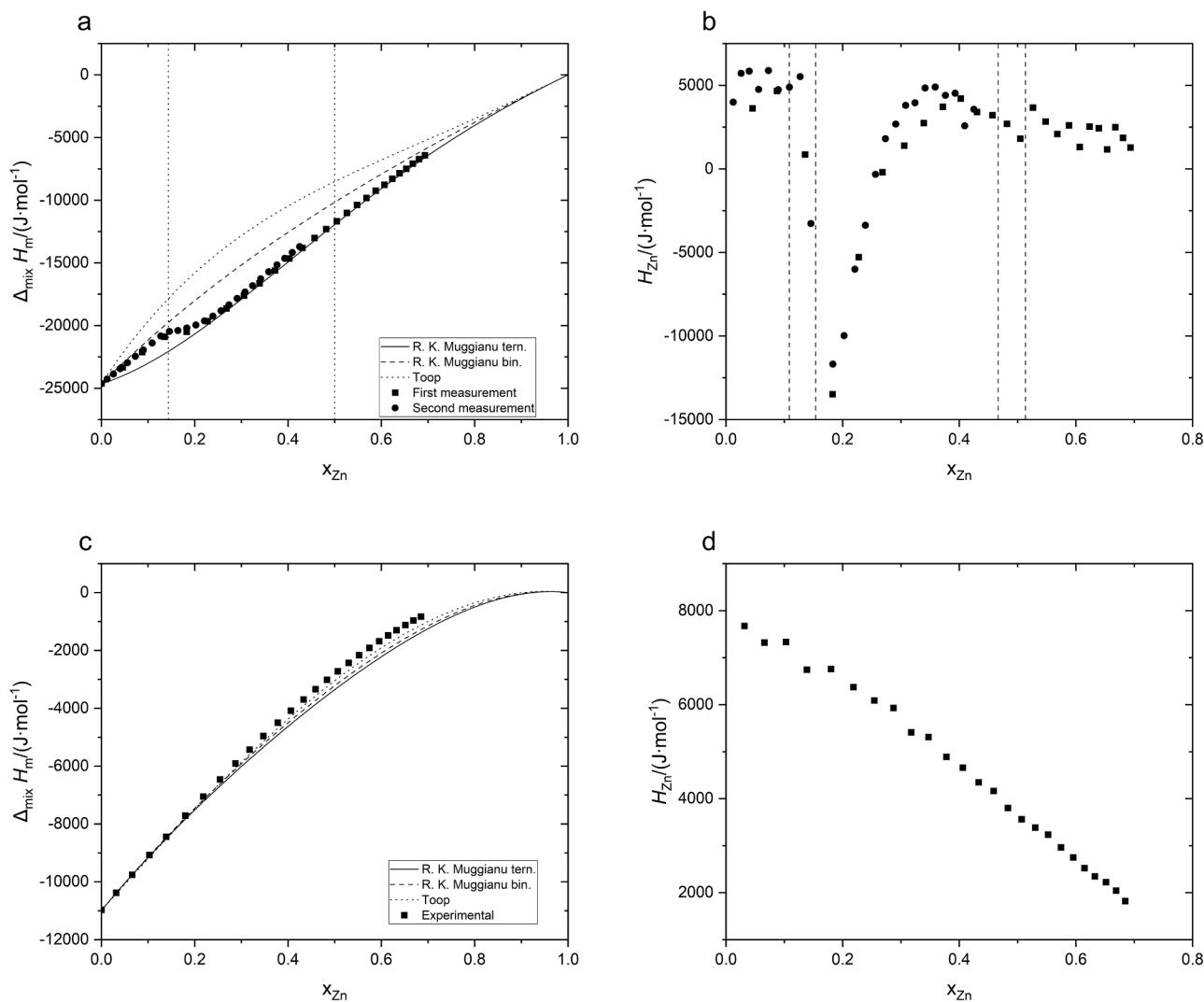


Fig. 3. Experimental integral (a and c) and partial (b and d) enthalpy of mixing for sections A ($\text{Li}_{45}\text{Sn}_{55}$) and B ($\text{Li}_{20}\text{Sn}_{80}$) determined at 823 K. Solid lines show data calculated with the RKM model (ternary), dashed lines the RKM model (binary) and dotted lines the Toop model. Vertical dotted lines (a) indicate phase boundaries. Vertical dashed lines (b) indicate liquidus limits.

(measurement series C, D, and E) and Fig. 5 (measurement series F, G, H, and I). Since the calculation is based on fully single-phase liquid alloys calculated values can only be compared to experimental values within these regions. The Iso-enthalpy plots modelled with Muggianu (ternary), Muggianu (binary) and Toop extrapolation are illustrated in Fig. 6.

4.3. Discussion

The performed measurements A-I can be roughly divided into three groups: In the first, Zn was dropped into liquid Li-Sn alloys (A and B; see Fig. 3 and Table S2). In the second, Li was dropped into liquid Sn-Zn alloys (C, D, and E; see Fig. 4 and Table S3). And in the third, Sn was

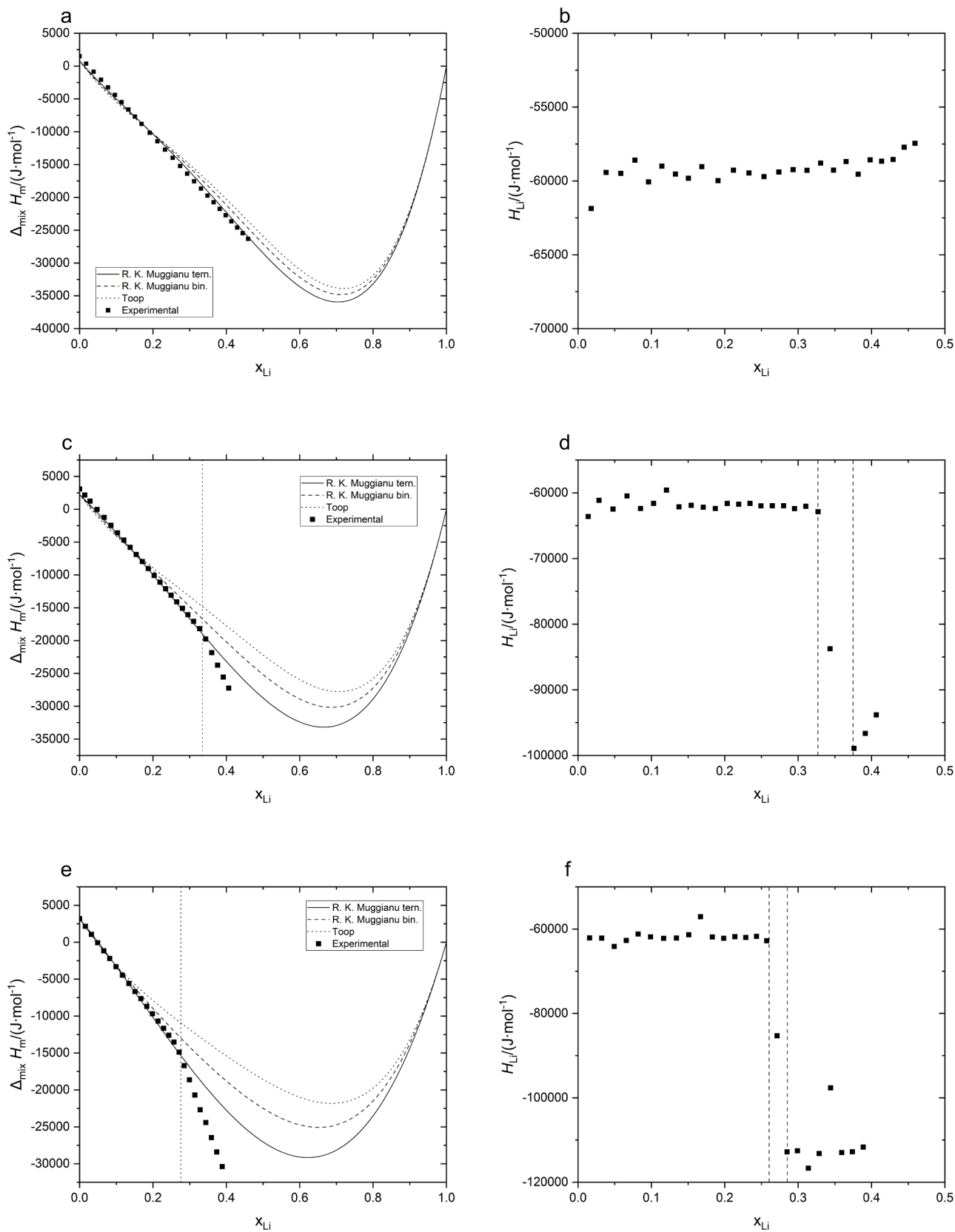


Fig. 4. Experimental integral (a, c, e) and partial (b, d, f) enthalpy of mixing determined at 823 K for sections C (Sn₉₀Zn₁₀), D (Sn₇₀Zn₃₀) and E (Sn₅₀Zn₅₀). Solid lines show data calculated with the RKM model (ternary), dashed lines the RKM model (binary) and dotted lines the Toop model. Vertical dotted lines (c, e) indicate phase boundaries. Vertical dashed lines (d, f) indicate liquidus limits.

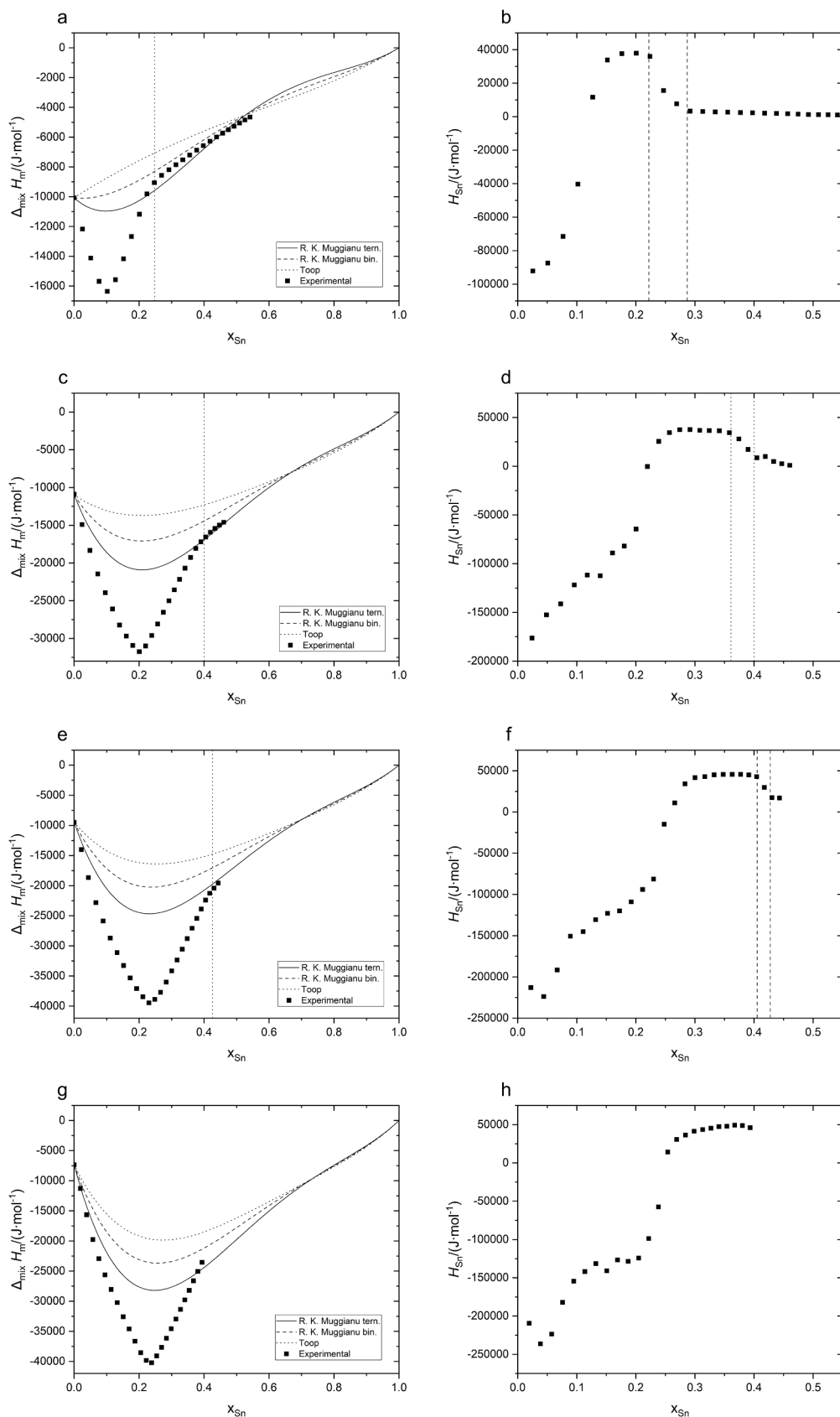


Fig. 5. Integral (a, c, e, g) and partial (b, d, f, h) enthalpy of mixing for sections F ($\text{Li}_{25}\text{Zn}_{75}$), G ($\text{Li}_{50}\text{Zn}_{50}$), H ($\text{Li}_{60}\text{Zn}_{40}$) and I ($\text{Li}_{70}\text{Zn}_{30}$). Solid lines show data calculated with the RKM model (ternary), dashed lines the RKM model (binary) and dotted lines the Toop model. Vertical dotted lines (a, c, e) indicate phase boundaries. Vertical dashed lines (b, d, f) indicate liquidus limits.

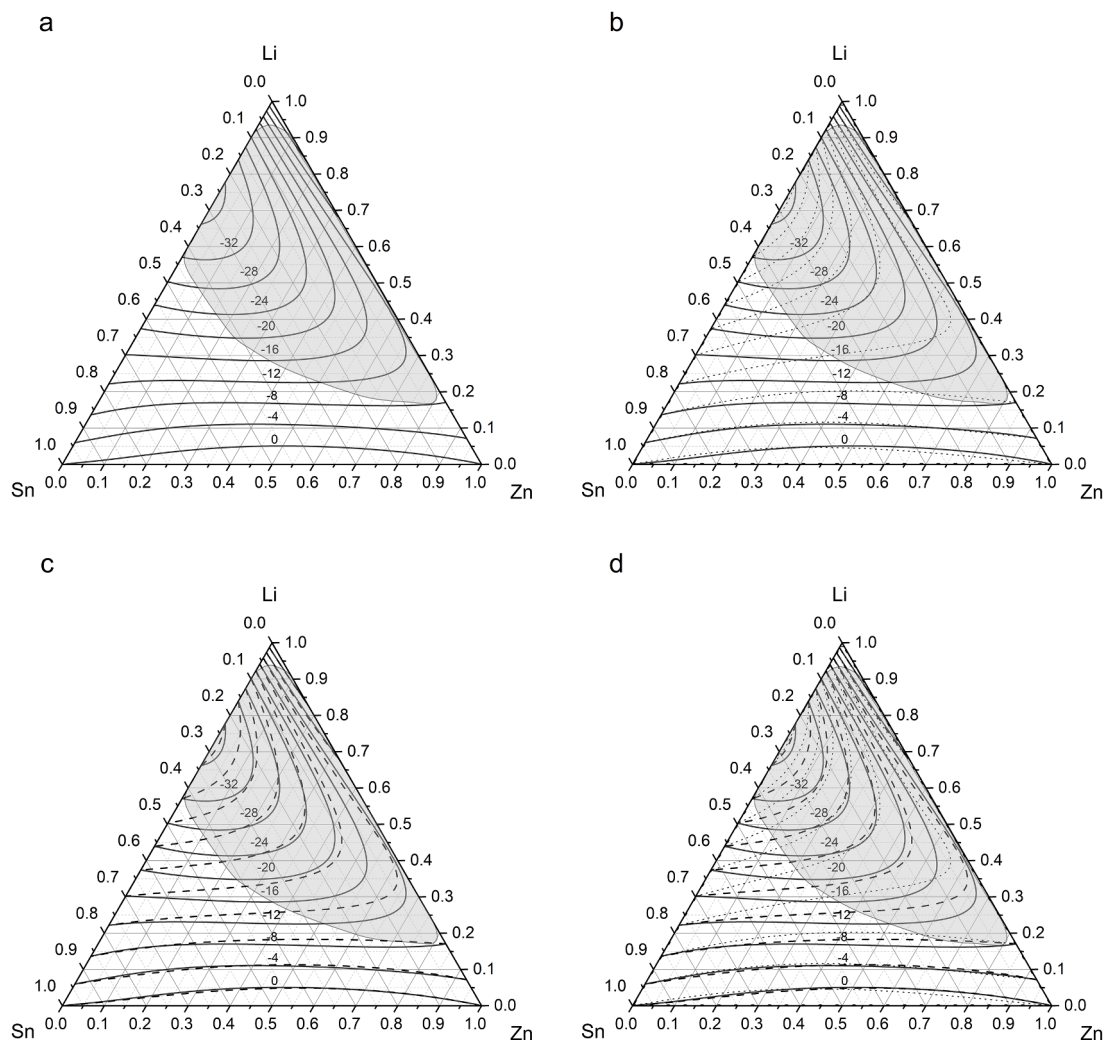


Fig. 6. Iso-enthalpy plots calculated with different extrapolation models. Redlich-Kister Muggianu fit with ternary interaction parameters (solid lines; a, b, c, d), Toop extrapolation (dotted lines; b, d), Redlich-Kister Muggianu extrapolation based on binary data (dashed lines; c, d). The gray area indicates the metastable monophase liquid state.

dropped into liquid Li-Zn alloys (F, G, H, and I; see Fig. 5 and Table S4).

Fig. 7 shows an isothermal section of the ternary system Li-Sn-Zn at 823 K we have calculated based on the thermodynamic data set published from Turchi et al. [25].¹ It indicates some areas of de-mixing of the liquid leading to a ternary miscibility gap. In addition, several two- and three-phase regions with liquid and binary Li-Sn and Li-Zn equilibrium phases are shown. No ternary phases were considered for this calculation.

Following, we discuss our experimental results and the course of the evaluated partial and integral enthalpy of mixing curves along the respective sections. First of all, according to the calculated phase diagram in Fig. 7, only sections B and C are situated in the fully liquid range. This is indeed confirmed by the enthalpy results which are plotted in Fig. 3, c,d and Fig. 4, a,b. Both sections are the only ones showing no kink in the integral values nor a jump point in the partial values. It must be stated at this point that thermodynamic state functions show constant partial values and linear slope of integral values along multi-phase regions. According to the calculation, section A crosses the miscibility gap at approx. 10 at.% Zn and comes back into the homogeneous liquid

¹ Gibbs energy descriptions of binary phases which do not belong to Li-Sn-Zn have been removed. They were erroneously introduced by the author taking binary data from ternary assessments of Al-Li-Zn and Cu-Sn-Zn.

region at approx. 55 at.% Zn. The partial enthalpy of mixing presented in Fig. 3b shows endothermic mixing at the beginning and a huge jump to exothermic values at approx. 10 at.% Zn. It comes back to slightly lower endothermic values than at the beginning at approx. 35 at.% Zn. A further small jump to less endothermic values can be observed at approx. 50 at.% Zn. Based on the calculated isotherm [25] this course of the curve can only partly be attributed to the liquid miscibility gap which is crossed by section A. Even though the first jump occurs at 10 at.% Zn it is too exothermic for liquid de-mixing and the enthalpy curve comes back to endothermic values much before 55 at.% Zn. The second jump occurs close to the end of the miscibility gap at 55 at.% Zn. The existence of a ternary compound $\text{Li}_3\text{Sn}_4\text{Zn}_2$ was reported by Stegmaier et al. [28], which is situated almost at the cross-section A. We have synthesized an alloy with the composition $\text{Li}_{33.3}\text{Sn}_{44.4}\text{Zn}_{22.2}$. For details about sample preparation see e.g., [14,36]. It was subjected to thermal analysis, the DTA curve is shown in Fig. 8. On heating no clear peak corresponding to full liquification can be observed, however, on cooling two clear peaks are visible at 823 ± 2 and 828 ± 2 K showing – may be undercooled – solidification. The higher temperature is clearly above 823 K, the temperature of the calorimeter cell. From this we conclude that the jump to exothermic partial enthalpy values along section A shown in Fig. 3b is attributed to the formation of a solid phase which could be the ternary compound $\text{Li}_3\text{Sn}_4\text{Zn}_2$. The sample was annealed at 573 K for 28 d after DTA measurement. A powder XRD analysis showed the presence of

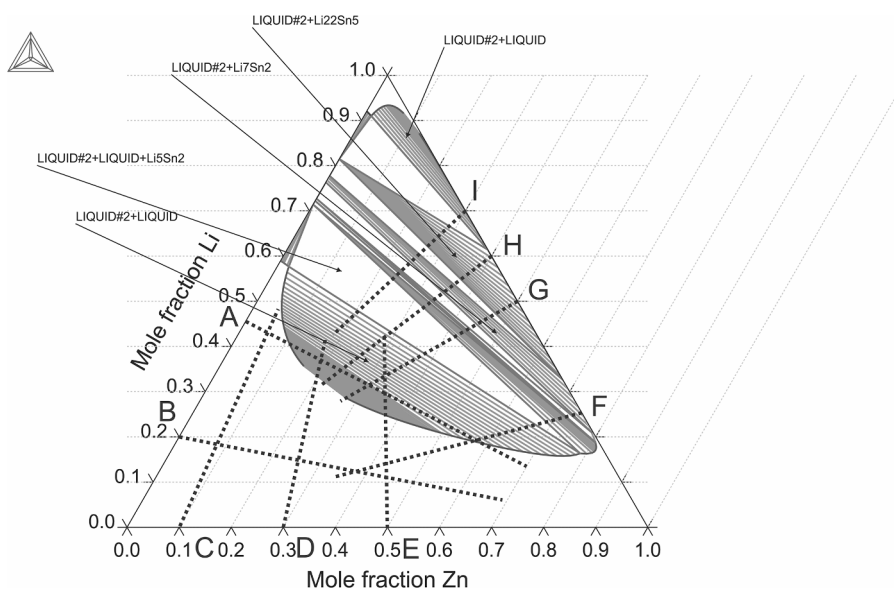


Fig. 7. Calculated version of the ternary system Li-Sn-Zn at 823 K. Based on data by Turchi et al. [25]. Measured sections (A, B, C, D, E, F, G, H, I) are indicated as dotted lines.

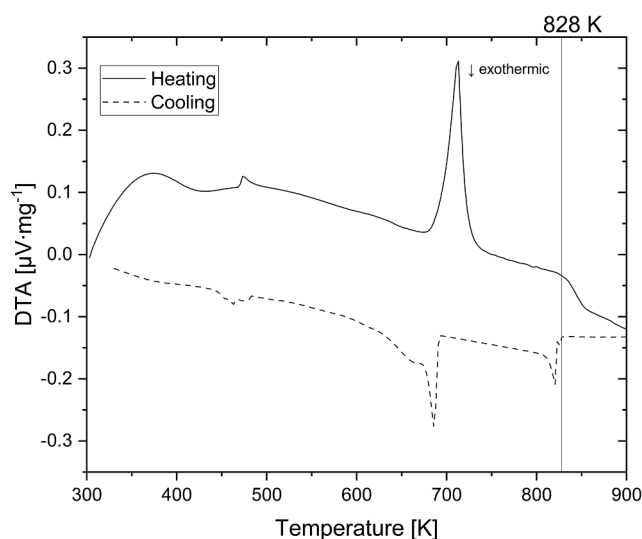


Fig. 8. DTA heating and cooling curve for $\text{Li}_{33.3}\text{Sn}_{44.4}\text{Zn}_{22.2}$. The measurement was performed with a heating/cooling rate of $5 \text{ K}\cdot\text{min}^{-1}$ in a dynamic Ar-flow of $20 \text{ ml}\cdot\text{min}^{-1}$.

$\text{Li}_3\text{Sn}_4\text{Zn}_2$ together with Sn and traces of Zn (see Figure S2 in the supplementary material). It must be noticed again that the assessment of Turchi [25], on which the calculated isotherm in Fig. 7 is based on, does not include ternary data.

For section A (Fig. 3a) at low Zn-concentration, before entering a multiple-phase field, the Muggianu extrapolation model seems to be more accurate whereas the Toop model fails to describe the experimental data. The Muggianu fit describes experimental data well at higher Zn-concentrations after the two-phase region. Section B is liquid over the whole composition range. The descriptions with the Muggianu model and the Muggianu fit match the experimental values very well, the Toop model fails at high Zn-concentration.

Sections C-E describe the behavior when Li is dropped into liquid Sn-Zn alloys. Generally, interactions between Sn-Zn in the liquid region are quite weak and endothermic, they have a maximum of about $3000 \text{ J}\cdot\text{mol}^{-1}$ at about $x_{\text{Zn}} = 0.6$ [24]. Lithium reacts strongly exothermic with

both Sn and Zn - this is also the case in sections C-E. Section C is in the single liquid phase region over the whole composition range. The Muggianu-fit well reproduces the experimental values, also the binary extrapolation models apply very well. Section D, shown in Fig. 4 c, d, reveals a kink in the course of the integral enthalpies and a jump point in the course of partial enthalpy values, both at approx. 35 at.% Li. This perfectly fits to the calculated isotherm shown in Fig. 7. A similar situation can be observed for section E, presented in Fig. 4 e,f. The kink and the jump, respectively, occur at approx. 25 at.% Li, again in excellent agreement with the calculated isotherm. Also, the partial enthalpy values of $100000\text{--}120000 \text{ J}\cdot\text{mol}^{-1}$ for Li after the jump are observed in both sections and indicate ending in the same multi-phase field. Quite constant partial enthalpies of mixing of about $-60000 \text{ J}\cdot\text{mol}^{-1}$ in the single-phase liquid are observed in all three sections C, D, and E. This liquid region is perfectly described by the Muggianu-fit, the extrapolation models show deviations to less exothermic values at higher Li-concentrations. The extension of the single liquid regions decreases from at least $x_{\text{Li}} = 0.45$ to $x_{\text{Li}} = 0.27$ from section C to E (see Table 3).

Sections F-I describe the mixing behavior when Sn is dropped into liquid Li-Zn alloys. While sections F, shown in Fig. 5b, starts at partial enthalpies of about $-100000 \text{ J}\cdot\text{mol}^{-1}$, the other ones (G, H, and I) start at partial enthalpies of mixing of about $-200000 \text{ J}\cdot\text{mol}^{-1}$ and additionally show small plateaus at about $-125000 \text{ J}\cdot\text{mol}^{-1}$. The partial values of all four sections show an endothermic plateau at approx. $45000 \text{ J}\cdot\text{mol}^{-1}$ before they come close to $0 \text{ J}\cdot\text{mol}^{-1}$ when finally entering the single-phase liquid region. The plateau at $45000 \text{ J}\cdot\text{mol}^{-1}$ is most probably attributed to the liquid miscibility gap; liquid de-mixing can cause endothermic partial values whereas the integral values are still exothermic. Based on equation (8):

Table 3
Limiting liquidus concentrations in the system Li-Sn-Zn at 823 K.

Section	A	B	C	D	E	F	G	H	I
Liquid to semi-liquid	$x_{\text{Zn}} = 0.11$	-	-	$x_{\text{Li}} = 0.33$	$x_{\text{Li}} = 0.27$	-	-	-	-
Semi-liquid to liquid	$x_{\text{Zn}} = 0.50$	-	-	-	-	$x_{\text{Sn}} = 0.28$	$x_{\text{Sn}} = 0.40$	$x_{\text{Sn}} = 0.43$	-

$$\Delta_{\text{mix}}H = x_{\text{Li}} \cdot \Delta_{\text{mix}}\bar{H}_{\text{Li}} + x_{\text{Sn}} \cdot \Delta_{\text{mix}}\bar{H}_{\text{Sn}} + x_{\text{Zn}} \cdot \Delta_{\text{mix}}\bar{H}_{\text{Zn}} \quad (8)$$

after transformation $\Delta_{\text{mix}}\bar{H}_{\text{Sn}}$ can be calculated from the integral enthalpy at the crossing point AE, see Fig. 1 respectively Table 2, and the partial enthalpy of Li and Zn at the respective concentrations. This provides us a value for $\Delta_{\text{mix}}\bar{H}_{\text{Sn}}$ within the liquid miscibility gap which can be compared to the experimental ones from the drops of Sn into Li-Zn alloys, sections F – I. The result of our calculation is $43500 \text{ J}\cdot\text{mol}^{-1}$ and confirms the experimental values of approx. $45000 \text{ J}\cdot\text{mol}^{-1}$.

For sections F, G, and H the Muggianu (tern.) model gives the best description for the integral enthalpies of mixing. Our results indicate that all measurements after the first drop of Sn are already in a multiphase region rather than a monophasic liquid and that there are several two- and three-phase fields on the pathway to Sn. The extension of the liquid miscibility gap rises from $x_{\text{Sn}} = 0.28$ to $x_{\text{Sn}} = 0.43$ and above with increasing Zn content (see Table 3). Section I seems to end up in the liquid miscibility gap.

As expected for all measured sections, the Muggianu model with ternary interaction parameters gives the best description of the integral mixing enthalpy, whereas the extrapolation models only partly sufficiently describe the ternary data. However, the Muggianu model gives a better description than the Toop model what is somewhat surprising since we have two similar and one dissimilar binary constituent system. The relatively small contribution of the ternary parameters 0M , 1M and 2M , nevertheless, is not a proof for real ternary interaction in a physical sense. It is rather a correction of the shortcoming of the Muggianu extrapolation model. In Fig. 6 a-d the integral enthalpy of mixing in the ternary system Li-Sn-Zn is presented as iso-enthalpy plots calculated based on Muggianu fit, and Muggianu and Toop model, respectively. Enthalpy values within the gray-shaded region represent the metastable monophasic liquid state. The mixing behavior in the ternary system is dominated by the binary Li-containing systems which both show a strongly exothermic minimum of the integral enthalpy, Li-Sn with $-37000 \text{ J}\cdot\text{mol}^{-1}$ at $x_{\text{Li}} = 0.8$ and Li-Zn with $-11700 \text{ J}\cdot\text{mol}^{-1}$ at $x_{\text{Zn}} = 0.6$. Accordingly, an enthalpy valley extends between the two binary minima and two ternary compounds, Li_2SnZn , reported by Schuster in [26] and Pobitschka et al. [27] and $\text{Li}_3\text{Sn}_4\text{Zn}_2$, reported by Stegmaier et al. [28], crystallize within this region. Surprisingly, according to the thermodynamic assessment of Turchi [25], exactly this part of the phase diagram is covered by a large liquid miscibility gap. Unfortunately, the author does not further discuss this special feature in his paper. There is no liquid miscibility described in the constituent binary systems and no ternary data are included in the assessment. Nevertheless, our experimental results seem to confirm the calculated isothermal section at 823 K (see Fig. 7) in a far extend. The combination of liquid miscibility and compound formation is known from syntectic reactions which rarely occur in binary systems. It is worth to mention at this point that Na-Zn [37], a binary system chemically similar to Li-Zn, shows a syntectic reaction forming NaZn_{13} .

5. Conclusions

Molar integral and partial enthalpies of mixing in the liquid Li-Zn and Li-Sn-Zn system were investigated at 823 K. The mixing behavior in the ternary system is dominated by the binary Li-containing systems which both show a strongly exothermic behavior. A detailed discussion of the data including a comparison with a calculated isothermal section at 823 K was made. Various extrapolation models of the binary data were compared with modelling using the ternary data. The experimental data significantly improved the modelling. In the experimental conditions, a considerable part of the system is covered by a liquid miscibility gap respectively by several 2- and 3-phase regions of liquid and solid phases. The phase diagrams of Li-Zn and Li-Sn-Zn in solid state are currently under investigation regarding crystal structures and phase equilibria.

CRedit authorship contribution statement

Lukas Fischer: Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Hans Flandorfer:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.123978>.

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