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Thermodynamic description of the CsBr–TbBr$_3$ system

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ABSTRACT

This work analyzed the thermodynamic properties and phase diagram of the CsBr–TbBr$_3$ system using the CALPHAD method. The phase diagram of the CsBr–TbBr$_3$ system, the thermodynamic properties of the Cs$_3$TbBr$_6$ compound and the enthalpies of mixing of the CsBr–TbBr$_3$ liquid at 1113 K are calculated. Comparison of calculated phase diagram and thermodynamic values with corresponding experimental data demonstrated that the present calculations based on the optimized parameters reproduce experimental data very well.

1. Introduction

Lanthanide metal halides and their mixtures with alkali metal halides play an important role in everyday life and in many industrial applications. They can be extracted and processed into metals, magnet alloys, oxides and other forms. Extraction and processing of lanthanides are largely based on molten salt technologies. CsBr–TbBr$_3$ is one of the key quasi-binary systems and the thermodynamics of the system can be used to investigate phase relations in multi-component systems relevant to lanthanide metal production by molten salt electrolysis. We have carried out the thermodynamic investigation on the TbBr$_3$ and MBr–TbBr$_3$ systems (M = Li, Na, K, Rb) [1–4]. Present paper is focused on the assessment of thermodynamic parameters of the CsBr–TbB$_3$ system using available phase diagram and thermodynamic data and thus it is a continuation of our systematic study on the thermodynamics of the TbBr$_3$-included molten salts.

2. Evaluation of experimental data in the literature

2.1. Phase diagram data

Using differential scanning calorimeter (DSC), Rycerz [5] has determined the phase diagram of the CsBr–TbBr$_3$ system over the whole composition range. Besides the liquid, CsBr and TbBr$_3$ solid phases, three intermediate compounds Cs$_3$TbBr$_6$, Cs$_3$Tb$_2$Br$_9$ and CsTb$_2$Br$_7$ existed in the CsBr–TbBr$_3$ system. Cs$_3$TbBr$_6$ was reported to undergo a solid phase transition at 728 K and to melt congruently at 1083 K with the corresponding enthalpies 2.1 and 15.15 kJ/(mol-cation). CsTb$_2$Br$_7$ melted incongruently, transformed to low temperature structural modification at 805 K and decomposed at 776 K. Cs$_3$Tb$_2$Br$_9$ melted incongruently at 879 K. Rycerz [5] reported two eutectics, which were located at the TbBr$_3$ mole fractions, $x_{\mathrm{TbBr_3}} = 0.095$ (865 K) and $x_{\mathrm{TbBr_3}} = 0.5623$ (808 K), respectively. No mutual solubility between solid state CsBr and TbBr$_3$ was detected.

There were not any other experimental phase diagram data about the CsBr–TbBr$_3$ system up till now.

The above mentioned information was used for the determination of the thermodynamic parameters in the present work, and an accuracy of about 3% [5] was used, since the experimental procedure was well prepared.

2.2. Thermodynamic data

Rycerz [5] measured the heat capacities and the enthalpies of transition and melting for the compound Cs$_3$TbBr$_6$ by using DSC measurements operated in a stepwise mode. The measured heat capacity data showed a break point in the temperature range 722–737 K, which is in good consistency with the reported solid–solid phase transition at 728 K [5]. This work employed the experimental heat capacity data and the enthalpies of transition and melting to optimize the Gibbs energy functions of Cs$_3$TbBr$_6$.

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By using a Calvet-type high temperature microcalorimeter, Rycerz and Gaune-Escard [6] have measured the molar enthalpies of mixing ΔH_{mix} at 1113 K for liquid MBr–TbBr$_3$ (M = Li–Cs) over the entire composition range. All the melts under investigation are characterized by negative enthalpies of mixing with a minimum shifted towards the alkali bromine-rich composition and located in the vicinity of $x_{\mathrm{TbBr_3}}\sim 0.3$–0.4, which showed that the complex species such as $[\mathrm{TbBr_6}]^{-3}$, $[\mathrm{TbBr_5}]^{-2}$, $[\mathrm{Tb_2Br_{11}}]^{-5}$, $[\mathrm{Tb_3Br_{10}}]^{-}$ exist in the MBr–TbBr$_3$ systems although the octahedral complexes $[\mathrm{TbBr_6}]^{-3}$ is always predominant in MBr-rich bromide liquid mixtures. The detail explanation can be found elsewhere [1–4,7,8]. These data were used during choice the thermodynamic model for the liquid phase, and the reported accuracy of about 6% [5] was accepted.

3. Thermodynamic models

3.1. Thermodynamic functions of components

The Gibbs energy function ${}^0G_i^{\phi}(T) = G_i^{\phi}(T) - H_i^{SER}$ for the component i (i = CsBr and TbBr$_3$) in the phase ϕ is expressed by an equation of the form:

$$ {}^0G_i^{\phi}(T) = a + bT + cT\ \ln\ T + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9} \qquad (1) $$

H_i^{SER} is the sum of the enthalpies of the elements at 298.15 K and 1 bar in their stable states (Stable Element Reference, denoted as SER). T is the absolute temperature. The ${}^0G_i^{\phi}(T)$ expressions can be given for several temperature ranges, where the coefficients a–h have different values. While the term gT^7 is only used for a liquid below the melting point and hT^{-9} for a solid above the melting point [9]. The values of these coefficients for CsBr were taken from SGTE Molten Salts Database, 1996 [10]. Those for TbBr$_3$ were from our previous work [1].

3.2. Liquid phase

Based on the characteristic of enthalpies of mixing of liquid MBr–TbBr$_3$ and for the sake of compatibility, the liquid phase was described with a two-sublattice ionic solution model [11], $(\mathrm{Cs^+})_P$:$(\mathrm{Br^-}, \mathrm{TbBr_6}^{-3}, \mathrm{TbBr_3})_Q$, and its Gibbs energy was expressed as follows:

$$ \begin{aligned} G_m^L - H^{SER} = {} & y_{\mathrm{Br^-}}\,{}^0G_{\mathrm{CsBr}}^L + y_{\mathrm{TbBr_6}^{-3}}\,{}^0G_{\mathrm{Cs_3TbBr_6}}^L + y_{\mathrm{TbBr_3}}\,{}^0G_{\mathrm{TbBr_3}}^L \\ & + RT(y_{\mathrm{Br^-}}\ \ln y_{\mathrm{Br^-}} + y_{\mathrm{TbBr_6}^{-3}}\ \ln y_{\mathrm{TbBr_6}^{-3}} \\ & + y_{\mathrm{TbBr_3}}\ \ln y_{\mathrm{TbBr_3}}) + {}^EG_m \end{aligned} \qquad (2) $$

where y is the site fraction, P and Q are the number of sites on each sublattice. ${}^0G_{\mathrm{CsBr}}^L$ is the molar Gibbs energy of the liquid CsBr from SGTE database [10], ${}^0G_{\mathrm{TbBr_3}}^L$ that of the liquid TbBr$_3$ from Ref. [1]. ${}^0G_{\mathrm{Cs_3TbBr_6}}^L$ the associated Cs$_3$TbBr$_6$ in the liquid state, which expressed by the following relation and to be evaluated in this work:

$$ {}^0G_{\mathrm{Cs_3TbBr_6}}^L = 3\,{}^0G_{\mathrm{CsBr}}^L + {}^0G_{\mathrm{TbBr_3}}^L + A_1 + B_1T \qquad (3) $$

${}^EG_m$ is the excess Gibbs energy, which depends on the interaction between the species within each sublattice. It was here described by a Redlich–Kister polynomial [12]:

$$ \begin{aligned} {}^EG_m = {} & y_{\mathrm{Br^-}}y_{\mathrm{TbBr_3}}[(a_0 + b_0T) + (y_{\mathrm{Br^-}} - y_{\mathrm{TbBr_3}})(a_1 + b_1T) \\ & + (y_{\mathrm{Br^-}} - y_{\mathrm{TbBr_3}})^2(a_2 + b_2T) + \cdots] \\ & + 3y_{\mathrm{TbBr_6}^{-3}}y_{\mathrm{TbBr_3}}[(a_0 + b_0T) + (y_{\mathrm{TbBr_6}^{-3}} - y_{\mathrm{TbBr_3}})(a_1 + b_1T) \\ & + (y_{\mathrm{TbBr_6}^{-3}} - y_{\mathrm{TbBr_3}})^2(a_2 + b_2T) + \cdots] \\ & + y_{\mathrm{Br}^{-3}}y_{\mathrm{TbBr_6}^{-3}}(c_0 + d_0T) \end{aligned} \qquad (4) $$

here the same interaction existing between the neutral and anionic species was adopted.

3.3. Cs$_3$TbBr$_6$ compounds

There are experimental data available for heat capacity of Cs$_3$TbBr$_6$ in a wide temperature range [5] and therefore heat capacity of this compound was described by Maier-Kelly equation $C_\mathrm{p} = c + dT + eT^{-2}$. The Gibbs energy of Cs$_3$TbBr$_6$ was expressed by the following equation:

$$ {}^0G_{\mathrm{Cs_3TbBr_6}}^S = A_2 + B_2T + C_2T\ \ln T + D_2T^2 + E_2T^{-1} \qquad (5) $$

where $C_2 = -c, D_2 = -d/2, E_2 = -e/2$ and they are to be evaluated from the experimental heat capacity data.

3.4. The Cs$_3$Tb$_2$Br$_9$ and CsTb$_2$Br$_7$ compounds

Since there were no experimental thermodynamic data, the compounds Cs$_3$Tb$_2$Br$_9$ and CsTb$_2$Br$_7$ were described with Neumann–Kopp rule and their Gibbs energies were expressed by the following expressions, respectively:

$$ {}^0G_{\mathrm{CsTb_2Br_7}}^{\mathrm{S}} = {}^0G_{\mathrm{CsBr}}^{\mathrm{S}} + 2\,{}^0G_{\mathrm{TbBr_3}}^{\mathrm{S}} + A_3 + B_3T \qquad (6) $$

$$ {}^0G_{\mathrm{Cs_3Tb_2Br_9}}^{\mathrm{S}} = 3\,{}^0G_{\mathrm{CsBr}}^{\mathrm{S}} + 2\,{}^0G_{\mathrm{TbBr_3}}^{\mathrm{S}} + A_4 + B_4T \qquad (7) $$

A_i and B_i (i = 3, 4) are connected with the enthalpy and entropy of formation from pure bromides in the solid state, which will be evaluated in the course of optimization.

4. Optimization procedure

The Thermo-Calc program PARROT [13] was used for the present optimization. And a stepwise optimization procedure was designed to ensure the reasonableness of the produced parameters. The step-by-step optimization procedure was utilized in this section.

Using the experimental heat capacity data from Ref. [5], the coefficients C_2, D_2, and E_2 in Eq. (5) were evaluated for both the low- and high-modification Cs$_3$TbBr$_6$. Then the coefficients A_2 and B_2 were considered to fit the solid–solid structural transition information of the compound. Thirdly, the parameters A_1 and B_1 in Eq. (3) and the parameters a_i, b_i (i = 0, 1) and c_1 in Eq. (4) for the liquid phase were optimized to fit the enthalpy of melting of the compound Cs$_3$TbBr$_6$, the experimental liquidus data [5] and the enthalpies of mixing [6]. The Gibbs energies of the intermediate compounds Cs$_3$Tb$_2$Br$_9$ and CsTb$_2$Br$_7$ were considered one by one in the forth step. Finally, the whole system was optimized using all the selected experimental data simultaneously. The parameters already obtained were changed a little in this step to achieve the best overall fit.

5. Results and discussion

The thermodynamic parameters finally resulting from this work are given in Table 1. The phase diagram of the CsBr–TbBr$_3$ system is calculated and shown in Fig. 1, together with the experimental phase diagram data. It can be seen that the present calculation accounts for the invariant temperatures quite well. In addition, most of the experimental phase diagram data [5] are well reproduced. While the calculated liquidus temperatures in the TbBr$_3$-rich side appear some difference from the data measured by [5]. Considering the difficulty of high temperature experimentation and the extreme reactivity of the lanthanide halides, this discrepancy can be accepted.

Fig. 2 shows the calculated heat capacities for the compound Cs$_3$TbBr$_6$ marked with the corresponding experimental data. The

Table 1
Summary of the thermodynamic parameters of the CsBr–$TbBr_3$ system according to the present optimization.[a]

Gibbs energy of pure CsBr:

$^{0}G^{L}_{\mathrm{CsBr}}$:
$-402734.374+201.067788T-48.9127T\ln T-0.0067376T^{2}-1.602\times10^{-9}T^{3}+53T^{-1}$ $(298.15<T<300)$
$-388650.221-115.252423T+3.3642595T\ln T-0.082589054T^{2}+1.4803351\times10^{-5}\times T^{3}-664182T^{-1}$ $(300<T<965)$
$-415340.193+384.308318T-75T\ln T$ $(965<T<3500)$

$^{0}G^{S}_{\mathrm{CsBr}}$:
$-420782.687+218.677187T-48.9127T\ln T-0.0067376T^{2}-1.602\times10^{-9}T^{3}+53T^{-1}$ $(298<T<910)$
$-382274.79-147.290427T+3.1206606T\ln T-0.036475451T^{2}+2.931918\times10^{-6}T^{3}-5169758T^{-1}$ $(910<T<2000)$
$-444694.747+415.191402T-75T\ln T$ $(2000<T<3500)$

Interaction parameters of the liquid phase in the CsBr–$TbBr_3$ system:
$a_0=-98962.3$, $b_0=45.67$; $a_1=-55980.04$, $b_1=57.61$; $c_0=-162865.23$, $d_0=88.74$

Gibbs energy of the associated Cs_3TbBr_6 in the liquid state:
$^{0}G^{L}_{\mathrm{Cs_3TbBr_6}}=3\,{}^{0}G^{L}_{\mathrm{CsBr}}+{}^{0}G^{L}_{\mathrm{TbBr_3}}+70540.45-67.77T$

Gibbs energy of the compound Cs_3TbBr_6 in low-temperature modification ($^{0}G^{S}_{\mathrm{Cs_3TbBr_6}}$):
$-2151661.59+741.407T-191.629306T\ln T-0.0648691551T^{2}-2188102.35T^{-1}$

Gibbs energy of the compound Cs_3TbBr_6 in high-temperature modification:
$-2136671.46+558.156T-165.806747T\ln T-0.0794548081T^{2}-545244.908T^{-1}$

Gibbs energy of the compound Cs_3TbBr_6 in liquid modification:
$3\,{}^{0}G^{L}_{\mathrm{CsBr}}+{}^{0}G^{L}_{\mathrm{TbBr_3}}+70540.45-67.77T$

Gibbs energy of the compound $CsTb_2Br_7$ in low-temperature modification ($^{0}G^{S}_{\mathrm{CsTb_2Br_7}}$):
$^{0}G^{S}_{\mathrm{CsBr}}+2\,{}^{0}G^{S}_{\mathrm{TbBr_3}}+8819.5-53.96T$

Gibbs energy of the compound $CsTb_2Br_7$ in high-temperature modification:
$^{0}G^{S}_{\mathrm{CsBr}}+2\,{}^{0}G^{S}_{\mathrm{TbBr_3}}+11181.4-56.89T$

Gibbs energy of the compound $Cs_3Tb_2Br_9$ ($^{0}G^{S}_{\mathrm{Cs_3Tb_2Br_9}}$):
$3\,{}^{0}G^{S}_{\mathrm{CsBr}}+2\,{}^{0}G^{S}_{\mathrm{TbBr_3}}-119351.05+26.5T$

[a] In J/mol. Temperature (T) in Kelvin. The Gibbs energy functions of CsBr are from the SGTE database [10]. The Gibbs energy functions of $Tbbr_3$ can be found in Ref. [1].

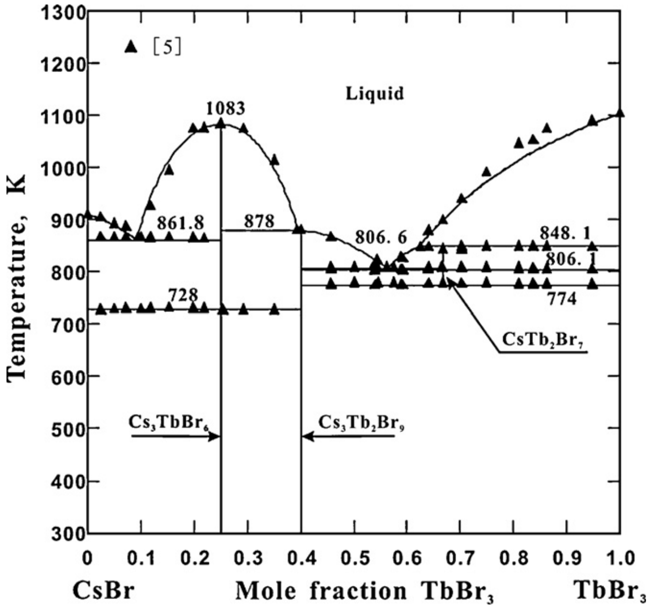

Fig. 1. Calculated CsBr–TbBr3 phase diagram compared with the measured data [5].

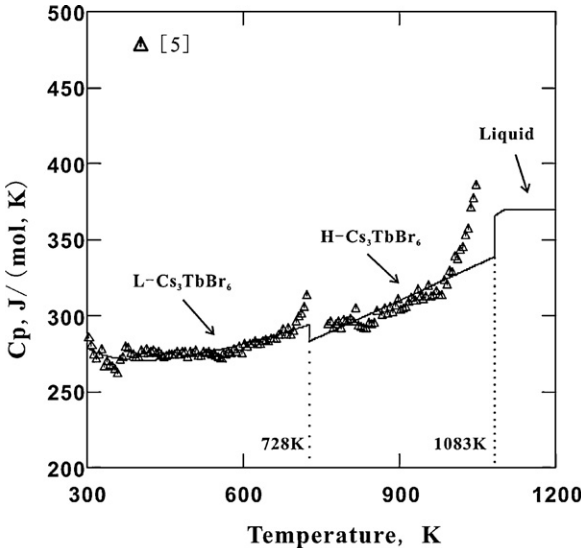

Fig. 2. Calculated heat capacity of the compound Cs3TbBr6 compared with the corresponding experimental data [5]. The heat capacities of the compound Cs3TbBr6 in liquid state are also calculated. 728 and 1083 K are the temperatures of the solid–solid phase transition and the fusion of the compound Cs3TbBr6, respectively.

Table 2
The thermodynamic properties of the compounds M_3TbBr_6 (M = Li, Na, K, Rb, Cs) and $CsTb_2Br_7$ together with literature data.[a]

Compound	$\Delta H_f(298)$	Phase transition		Melting		Reference
		T_{tr}	ΔH_{tr}	T_{melt}	ΔH_{melt}	
Li_3TbBr_6	−475513.7			785	5910	[3]
Na_3TbBr_6	−483193.1	745				[1]
K_3TbBr_6	−495934.5	691	800	983	5090	[2]
Rb_3TbBr_6	−511480.6	728	1946	1047	14855	[4]
Cs_3TbBr_6		728 ± 2	2100	1083 ± 3	15150	[5]
	−525839.2	728	2109	1083	14942	This work
$CsTb_2Br_7$				806 ± 3		[5]
		787		805		This work

[a] In J/(mol-cation). Temperature (T) in Kelvin.

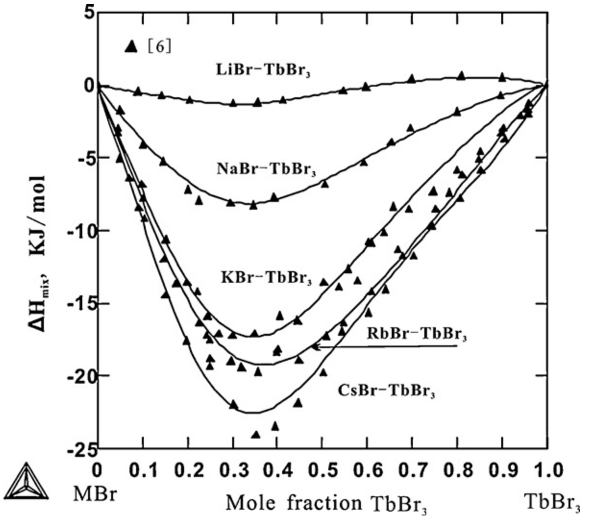

Fig. 3. Calculated enthalpy of mixing for the MBr–TbBr3 (M = alkali metal) liquid at 1113 K compared with experimental values [6]. The reference states are liquid MBr and liquid TbBr3.

agreement is good within the estimated experimental uncertainties, except for some deviation at the vicinity of transition temperatures. Table 2 shows the calculated thermodynamic properties of Cs_3TbBr_6 and $CsTb_2Br_7$. Fig. 3 compares the calculated enthalpies of mixing of CsBr–$TbBr_3$ liquid mixtures at 1113 K with the corresponding experimental data [6], a good agreement is obtained. The thermodynamic properties of M_3TbBr_6 (M = Li, Na, K, Rb) and the enthalpies of mixing of MBr–$TbBr_3$ liquid at 1113 K, based on our previous assessments [1–4] are also listed in Table 2 and Fig. 3, respectively. The major conclusions can be draw from Table 2 and Fig. 3: (1) the enthalpies of formation of the compounds M_3TbBr_6 (M = Li, Na, K, Rb, Cs) at 298.15 K from pure bromides in the solid state decrease as the ionic radius of the alkali metal**,** (2) the compounds M_3TbBr_6 (M = Li, Na, K, Rb, Cs) existed in all the MBr–$TbBr_3$ system, while only the compounds K_3TbBr_6, Rb_3TbBr_6 and Cs_3TbBr_6 have both high-temperature and low-temperature modifications and melt congruently. Their congruent melting temperatures and the relative enthalpies are in the sequence $K_3TbBr_6 < Rb_3TbBr_6 < Cs_3TbBr_6$, *i.e.*, increase as the ionic radius of the alkali metal, (3) for all the MBr–$TbBr_3$ system, the enthalpies of mixing show a minimum at compositions $x_{TbBr_3} \approx 0.3–0.4$. The absolute values of these negative enthalpies also increase with the ionic radius of the alkali metal. Gaune-Escard et al. [7,8] have found that the ionic radius of the alkali metal influences the magnitude of mixing enthalpy, the smaller the ionic radius, the smaller the absolute value of mixing enthalpy. The present investigated MBr–$TbBr_3$ liquid mixtures are in consistence with this general regularity. Gaune-Escard et al. [7,8] and our previous work [1–4] have also explained the relation between the composition location ($x_{TbBr_3} \approx 0.3–0.4$) of the minimum of these enthalpies and a short range order around the M_3TbBr_6 composition in liquid phase. The more negative enthalpies of mixing of the MBr–$TbBr_3$ systems should connect with the more strong attractive forces between M^+ and $TbBr_6{}^{-3}$, thus the higher stability, the higher melting points and higher enthalpies of melting of the compounds K_3TbBr_6, Rb_3TbBr_6 and Cs_3TbBr_6.

6. Conclusions

The thermodynamic assessment of the CsBr–$TbBr_3$ system was carried out by the CALPHAD technique. A two-sublattice ionic solution model, $(Cs^+)_P$:$(Br^-$, $TbBr_6{}^{-3}$, $TbBr_3)_Q$ was used to describe the liquid phase. The phase transitions and decompositions of Cs_3TbBr_6, $CsTb_2Br_7$ and $Cs_3Tb_2Br_9$ were taken into account. The Gibbs energies of the Cs_3TbBr_6 compound were optimized. A set of reasonable and self-consistent thermodynamic parameters were obtained. The calculated phase diagram of the CsBr–$TbBr_3$ system, the heat capacity of the compound Cs_3TbBr_6 and the enthalpies of mixing of the CsBr–$TbBr_3$ liquid at 1113 K showed good agreement with the corresponding experimental data. The similarities and the changing trends of the thermodynamic properties of M_3TbBr_6 (M = Li, Na, K, Rb, Cs) and the enthalpies of mixing of MBr–$TbBr_3$ melts were compared.

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