



A thermodynamic description of the KBr–EuBr₂ system



Weiping Gong^{a,*}, Marcelle Gaune-Escard^b

^a Laboratory of Electronic Functional Materials, Huizhou University, Huizhou 516001, Guangdong, PR China

^b Ecole Polytechnique, Mecanique Energetique, Technopole De Chateau-Gombert, 5 Rue Enrico Fermi, 13453 Marseille Cedex 13, France

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ABSTRACT

Critical thermodynamic description on KBr–EuBr₂ system was carried out by CALPHAD method. The thermodynamic parameters of the pure KBr and EuBr₂ compounds were taken from the SGTE recommended database and the authors' previous assessment, respectively. A two-sublattice ionic solution model for the liquid, denoted as (K⁺)_p:(Br⁻, EuBr₄⁻², EuBr₂)_Q, was employed to represent phase diagram and enthalpy of mixing data. To reach a self-consistent thermodynamic description for the constituent phases in the system, the experimental heat capacity data of the intermediate compounds K₂EuBr₄ and KEu₂Br₅ were evaluated.

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1. Introduction

Rare earth halide metals and their mixtures with alkali halides are important for industrial electrolytic process where they have been used for the production of the corresponding rare earth metals or as additives to improve the electrolytic production of light metals. The thermochemical parameters are required for the understanding the electrolytic process and hence prediction of the rare earth metals output. The data are also needed for predicting the behavior of multi-component metal halide systems.

Until recently, there were very few experimental studies reported in the literature for the rare earth halides. In order to identify the thermodynamic, physicochemical and structural properties of rare earth metal halides and their mixtures with alkali metal halides, several investigations have been or are being conducted with a variety of experimental methods, such as high temperature direct calorimetry, differential scanning calorimetry (DSC), X-rays analysis (XRD), electrical conductivity measurements, Raman spectroscopy and neutron diffractions, and also theoretical approaches including molecular dynamic calculations and computer coupling of phase diagrams and thermochemistry (CALPHAD). This paper deals with the KBr–EuBr₂ molten salt mixtures by using the CALPHAD technology, aims to provide the validation of result based on the experimental literature which, mainly concentrated on the liquid/solid equilibria and thermodynamic properties of KBr–EuBr₂ system, and to provide a set of consistent

thermodynamic parameters which can set up a reasonable phase diagram and predict the not-measured or “un-measurable” properties. Critical evaluation on the measured data and thus removal of systematic errors, probe for the best methods is also expected.

2. Evaluation of experimental data from the literature

Phase diagram of KBr–EuBr₂ quasi-binary system was established for the first time by Rycerz et al. [1] on basis of reproducible DSC combined with the electrical conductivity, spectroscopy measurement and the Tamman method. The system exhibits three eutectics and three stoichiometric compounds. The compound K₂EuBr₄ was found to melt congruently at 834 K. KEuBr₃, underwent a solid–solid phase transition at 810 K and decomposed peritectically at 846 K. KEu₂Br₅ melt congruently at 880 K. The composition of the three eutectic mixtures, x(EuBr₂) = 0.318, 0.433 and 0.789, respectively, were determined by the Tamman method. The respective eutectic temperatures were 829, 811 and 854 K. The mutual solubility between KBr and EuBr₂ was very limited so that it was ignored when carrying out Tamman method to evaluate the eutectic compositions. Table 1 lists the invariant reaction temperature and composition reported by Rycerz et al. [1] and assessed by the present authors considering the peak onsets of [1] on heating only. In the work of Rycerz et al. [1], the liquidus lines and melting temperatures as well as the invariant reactions were mainly based on the thermal effects in the heating curves. These data were considered to be reliable and, therefore, utilized in the present modelling.

With a Calvet-type high-temperature microcalorimeter, Rycerz et al. [2] measured the molar mixing enthalpy of liquid KBr–EuBr₂,

* Corresponding author. Tel.: +86 752 2527271.

E-mail address: gwp@hzu.edu.cn (W. Gong).

Table 1
Comparison between the calculated and experimental invariant points in the KBr–EuBr₂ system^a.

Equilibrium and type	Invariant points(x_{LaBr_3} , $T(\text{K})$)	Reference
Liquid $\xrightarrow{\text{Ec}}$ KBr + K ₂ EuBr ₄	(0.318, 829)	[1]
	(0.29, 826)	[This work]
Liquid $\xrightarrow{\text{melt}}$ K ₂ EuBr ₄	$T = 834$	[1,3]
	$T = 828$	[This work]
Liquid + KEu ₂ Br ₅ $\xrightarrow{\text{Pc}}$ H–KEuBr ₃	$T = 846$	[1]
	$T = 831$	[This work]
Liquid $\xrightarrow{\text{Ec}}$ K ₂ EuBr ₄ + KEuBr ₃	(0.43, 811)	[1]
	(0.40, 822)	[This work]
H–KEuBr ₃ $\xrightarrow{\text{Tr}}$ L–KEuBr ₃	$T = 811$	[1]
	$T = 810$	[This work]
Liquid $\xrightarrow{\text{melt}}$ KEu ₂ Br ₅	$T = 880$	[1,3]
	$T = 878$	[This work]
Liquid $\xrightarrow{\text{Ec}}$ KEu ₂ Br ₅ + EuBr ₂	(0.79, 854)	[1]
	(0.81, 853)	[This work]

^a In mole fraction, T in Kelvin, Ec: eutectic reaction, Pc: peritectic, Tr: phase transformation, H: high temperature structure and L: low temperature structure.

$\Delta_{\text{mix}}H$ at 1050 K over the entire composition range. The investigated melts were characterized by negative enthalpy with a minimum value. The minimum point was not found to shift pronouncedly towards either KBr or EuBr₂-rich composition. Rycerz et al. [2] also measured the electrical conductivity of all MBr–EuBr₂ liquid mixtures over the entire composition by platinum electrodes with conductivity meter Tacussel CD 810. The investigated KBr–EuBr₂ melts shows positive electrical conductivity and the broad minimum on the deviation curves from the Kuroda equation is located at about $x(\text{EuBr}_2) = 0.35$.

Using DSC and electrical conductivity methods, measurements of heat capacity and electrical conductivity were performed on K₂EuBr₄ and KEu₂Br₅ compounds [3]. The measured heat capacities for both compounds were used to evaluate their Gibbs energies. Some data above the melting temperatures were also reported, which is helpful for determining the thermodynamic properties of liquid.

3. Thermodynamic models

The Gibbs energy function ${}^\circ G_i^\Phi(T) = G_i^\Phi(T) - H_i^{\text{SER}}$ for the component i ($i = \text{KBr}, \text{EuBr}_2$) in the phase Φ is expressed:

$${}^\circ G_i^\Phi(T) = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9}, \quad (1)$$

where H_i^{SER} is the molar enthalpy of formation of the compound i at 298.15 K and 1 bar in its standard element reference (SER) state, and T is the absolute temperature. The last two terms in Eq. (1) are used only outside the ranges of stability [4], the term gT^7 for a liquid below the melting point and hT^{-9} for solid phases above the melting point.

Table 2
Summary of the thermodynamic parameters of the KBr–EuBr₂ system according to the present optimization^a.

Liquid: $a_0 + b_0T = -15704.6 - 4.29T$; $a_1 + b_1T = -7296.5 + 4.93T$; $c_0 = 6706$
${}^\circ G_{\text{K}_2\text{EuBr}_4}^{\text{L}} = -1865830.1 + 3025.5T - 262.28 \ln T$ ($828 < T < 6000$)
${}^\circ G_{\text{K}_2\text{EuBr}_4}^{\text{S}} = -1607739.2 + 613.56T - 134.02T \ln T - 0.059T^2 - 1324915.7T^{-1}$ ($298.15 < T < 828$)
${}^\circ G_{\text{KEu}_2\text{Br}_5}^{\text{S}} = -1992766.3 + 992.03T - 196.41T \ln T - 0.0423328T^2 + 122324.32T^{-1}$ ($298.15 < T < 878$)
${}^\circ G_{\text{KEuBr}_3}^{\text{S}} = {}^\circ G_{\text{KBr}}^{\text{S}} + {}^\circ G_{\text{EuBr}_2}^{\text{S}} - 16422 + 4.83T$

^a In J/mol. Temperature (T) in Kelvin. The Gibbs energies of KBr Molten salts database assessed by FactSage, Montreal Canada, and adopted by SGTE in May 1993 and can be found in [6], those of EuBr₂ from [7].

In the present work, the Gibbs energy functions of pure KBr, ${}^\circ G_{\text{KBr}}^{\text{L}}$ and ${}^\circ G_{\text{KBr}}^{\text{S}}$, were assessed by FACT, Montreal Canada, and adopted by SGTE in May 1993 [5], and can be found in [6]. The Gibbs energy functions of EuBr₂, ${}^\circ G_{\text{EuBr}_2}^{\text{L}}$ and ${}^\circ G_{\text{EuBr}_2}^{\text{S}}$, were taken from the authors' previous work [7].

For the liquid phase, a regular substitutional solution model, $(\text{M}^+, \text{Eu}^{+2})_{\text{p}}(\text{Br}^-)_{\text{Q}}$, where $\text{M} = \text{Li}$ or Na , has been successfully applied to describe the liquid phase in the LiBr–EuBr₂ and NaBr–EuBr₂ systems [7]. Because of the structural similarity between the alkali bromides, the regular substitutional solution model should be applicable to the liquid phase in the KBr–EuBr₂ system. However, the difficulties arose when the experimental phase diagram and thermodynamic data at higher EuBr₂ content were considered. By considering the structural characteristics of various lanthanide halide and alkali halide mixtures as well as the tetrahedral MeCl_4^{-2} type complexes existing in the $\text{MCl} - \text{MeCl}_2$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Me} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cd}, \text{Pb}$) mixtures [8–11], the complex specie EuBr_4^{-2} may be formed in the liquid KBr–EuBr₂. And more, the location of minimum on the deviation curve of KBr–EuBr₂ liquid system at $x(\text{EuBr}_2) = 0.35 - 0.50$ suggests the presence of EuBr_4^{-2} ($x(\text{EuBr}_2) = 0.33$) complex ions [2], $(\text{K}^+)_{\text{p}}(\text{Br}^-, \text{EuBr}_4^{-2}, \text{EuBr}_2)_{\text{Q}}$ was adopted in the present work. P and Q were the number of cation and anion sites, respectively, which vary with the composition:

$$\text{P} = \sum \gamma_i(-\gamma_i) = y_{\text{Br}^-} + 2y_{\text{EuBr}_4^{-2}}, \quad (2)$$

$$\text{Q} = \sum \gamma_j \gamma_j = \gamma_j = 1, \quad (3)$$

where y_i and γ_i , y_j and γ_j represented the site fraction and charges of anion i and cation j , respectively. The Gibbs energy for liquid was expressed by the following equation:

$$\begin{aligned} G_m^{\text{L}} - H^{\text{SER}} &= y_{\text{Br}^-} {}^\circ G_{\text{KBr}}^{\text{L}} + y_{\text{EuBr}_4^{-2}} {}^\circ G_{\text{K}_2\text{EuBr}_4}^{\text{L}} + y_{\text{EuBr}_2} {}^\circ G_{\text{EuBr}_2}^{\text{L}} \\ &+ RT(y_{\text{Br}^-} \ln y_{\text{Br}^-} + y_{\text{EuBr}_4^{-2}} \ln y_{\text{EuBr}_4^{-2}} + y_{\text{EuBr}_2} \\ &\times \ln y_{\text{EuBr}_2}) + {}^E G_m \end{aligned} \quad (4)$$

in which H^{SER} is the abbreviation of $x_{\text{KBr}} H_{\text{KBr}}^{\text{SER}} + x_{\text{EuBr}_2} H_{\text{EuBr}_2}^{\text{SER}}$, R is the gas constant, x_{KBr} and x_{EuBr_2} are the mole fractions of KBr and EuBr₂, respectively. ${}^\circ G_{\text{K}_2\text{EuBr}_4}^{\text{L}}$ is the Gibbs energy of the associated K₂(EuBr₄) in liquid state. It is noteworthy that the heat capacities above the melting temperatures of compounds K₂EuBr₄ can be used to evaluate the thermodynamic properties of liquid phase. With the heat capacity data available, the Gibbs energy of associated K₂(EuBr₄) in liquid state can be described by the following expression:

$${}^\circ G_{\text{K}_2\text{EuBr}_4}^{\text{L}} = A_1 + B_1T + C_1T \ln T + D_1T^2 + E_1T^{-1}. \quad (5)$$

The A_1 , B_1 , C_1 , D_1 and E_1 were to be optimized coefficients in the present work.

${}^E G_m$ in Eq. (4) was the excess Gibbs energy of liquid phase. In order to perform the thermodynamic optimization practically, the assumption [12,13] that the same interaction exists between the neutral and anionic species was adopted, and the number of independent interaction parameters was thus remarkably reduced. And more, an additional interaction parameter between Br^- and EuBr_4^{-2}

was introduced to avoid unrealistic immiscibility in the region between KBr and K_2EuBr_4 . Therefore, the excess Gibbs energy was written as follows:

$$\begin{aligned} {}^E G_m = & y_{Br^-} y_{EuBr_2} [a_0 + b_0 T + (y_{Br^-} - y_{EuBr_2})(a_1 + b_1 T) \\ & + (y_{Br^-} - y_{EuBr_2})^2 (a_2 + b_2 T) + \dots] + 2 y_{EuBr_4^{-2}} y_{EuBr_2} [a_0 \\ & + b_0 T + (y_{EuBr_4^{-2}} - y_{EuBr_2})(a_1 + b_1 T) \\ & + (y_{EuBr_4^{-2}} - y_{EuBr_2})^2 (a_2 + b_2 T) + \dots] + y_{Br^-} y_{EuBr_4^{-2}} (c_0 + d_0 T). \end{aligned} \quad (6)$$

a_i, b_i ($i = 0, 1$), c_0 and d_0 were to be optimized coefficients.

With the experimental heat capacity values available, the Gibbs energies of K_2EuBr_4 and KEu_2Br_5 can be expressed relative to the SER state by the following equations:

$${}^{\circ} G^S = A_2 + B_2 T + C_2 T \ln T + D_2 T^2 + E_2 T^{-1}. \quad (7)$$

The coefficients C_2 , D_2 and E_2 can be obtained from the heat capacities values.

Since no experimental thermodynamic data were available, the $KEuBr_3$ compound was described by the Neumann–Kopp rule. Thus, its' Gibbs energy function was given by:

$${}^{\circ} G_{KEuBr_3}^S = {}^{\circ} G_{KBr}^S + {}^{\circ} G_{EuBr_2}^S + A_3 + B_3 T. \quad (8)$$

A_3 and B_3 were connected with the enthalpy and entropy of formations of the compound $KEuBr_3$ in the solid state, which were to be evaluated in the course of optimization.

4. Optimization procedure

The Thermo-calc software package [14] was used to optimize the thermodynamic parameters related to the considered system. The critically selected experimental data were employed with a certain weight, which can be changed systematically until most of the experimental data were accounted for within the claimed uncertainty limits.

Optimization was started with the compounds K_2EuBr_4 and KEu_2Br_5 . Based on the measured heat capacities, the numerical values of the C_2 , D_2 and E_2 coefficients in Eq. (7) describing the Gibbs energy functions of both compounds can be obtained. Once C_2 , D_2 and E_2 for the two compounds have been estimated, the coefficients A_2 and B_2 in Eq. (7) can be evaluated from the measured phase diagram data. The obtained coefficients as well as the

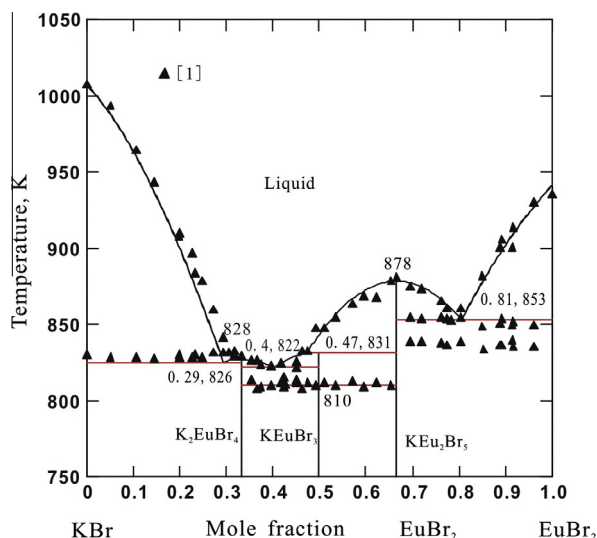


Fig. 1. Calculated phase diagram of KBr–EuBr₂ system, compared with the measured data from literature [1].

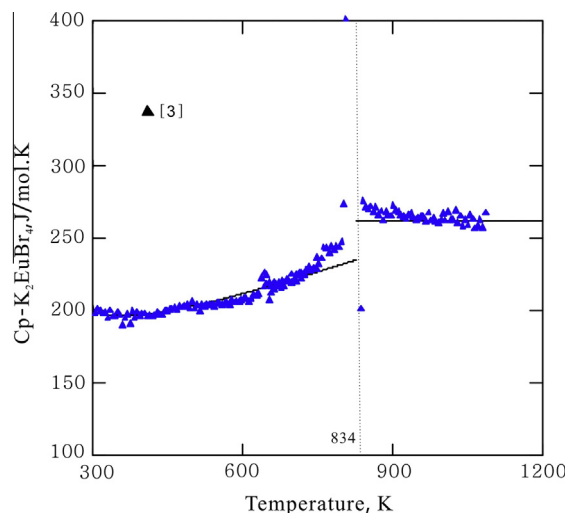


Fig. 2. Calculated heat capacity of K_2EuBr_4 compared with the experimental data [3].

calculated thermodynamic properties for the compounds were subjected to the further optimization.

Because there were a lot of experimental data, the critical description on the liquid phase was the most important for the successful optimization. In the present thermodynamic modeling, the measured heat capacities for liquid K_2EuBr_4 were used to preliminarily assess the Gibbs energy of associated $K_2(EuBr_4)$ in liquid, which was expressed by Eq. (5). The well measured liquidus line in the wide temperature and composition ranges [1], the well measured mixing enthalpy of liquid KBr–EuBr₂ [2] were employed to optimize the thermodynamic interactive parameters. Because the heat capacity of liquid phase is an “average” of liquid KBr, EuBr₂ and associated K_2EuBr_4 and the change of thermodynamic interactive parameters of liquid phase will change the equilibrium site fractions of Br[−], EuBr₄^{−2}, and EuBr₂, and thus change the contributions of each of them to the total Cp, in consequence, the preliminarily obtained Gibbs energy of associated $K_2(EuBr_4)$ and the interactive thermodynamic parameters of liquid phase should be evaluated together to get the best description of the liquid.

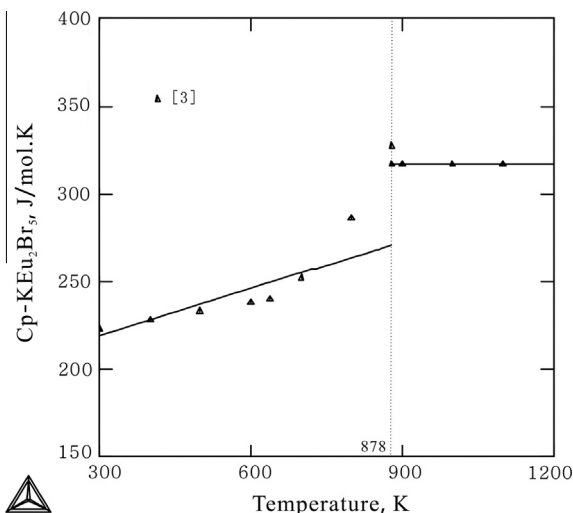


Fig. 3. Calculated heat capacity of KEu_2Br_5 compared with the experimental data [3].

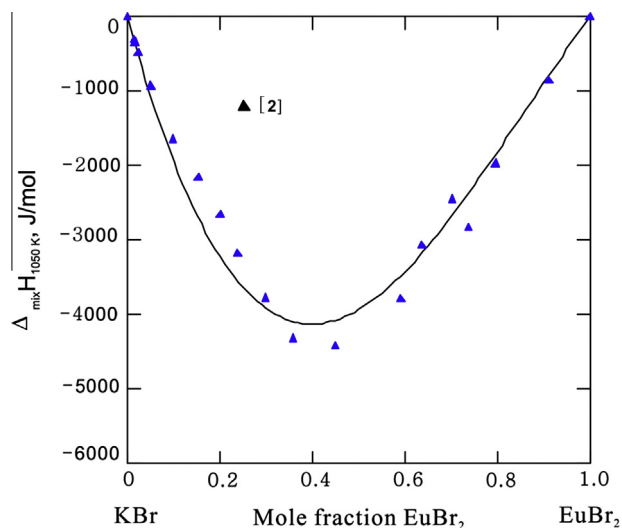


Fig. 4. Calculated mixing enthalpy of KBr–EuBr₂ liquid at 1050 K compared with the experimental values [2]. The reference states are liquid KBr and EuBr₂.

All the thermodynamic parameters were finally evaluated together and slight adjustments were made to give the best description of the system.

5. Results and discussion

The finally optimized thermodynamic parameters of KBr–EuBr₂ binary system are listed in Table 2. The KBr–EuBr₂ phase diagram calculated using this set of thermodynamic parameters is shown in Fig. 1. It can be seen, the calculated eutectic reactions, liquid → KBr + K₂EuBr₄ and liquid → EuBr₂ + KEu₂Br₅ reproduce the corresponding experimental data very well. The present calculated temperatures for the eutectic reaction, liquid → KEu₂Br₅ + K₂EuBr₄ as well as the incongruent melting of KEuBr₃ are 822 and 831 K, which are about 10–15° different with the reported temperatures. The optimization was carried out to remove this discrepancy, but the decomposition of KEu₂Br₅ and K₂EuBr₄ at some lower temperature were detected by using slightly modified thermodynamic parameters. Thus, the present calculation prefers the above mentioned temperatures. The weak DSC thermal effect at about 838 K (less than 0.7 kJ/mol) was reported in the reference [1] for all mixtures in the composition range 0.7 < x < 1, which cannot be explained at the present time.

Figs. 2 and 3 compare the calculated heat capacities of compounds K₂EuBr₄ and KEu₂Br₅ marked with the corresponding experimental data [3], respectively. The good agreement is

obtained, which proves the stability of the compounds and is in consistent with the phase diagram information.

Fig. 4 is the calculated mixing enthalpies of liquid at 1050 K. The most minimum value is found at about 40 mol.% EuBr₂, which shifted towards the KBr-rich compositions confirming the existence of EuBr₄²⁻ cluster. The fit to the measured data is excellent.

6. Conclusions

In the paper, a sub-lattice ionic solution model, (K⁺)_p(Br⁻, EuBr₄²⁻, EuBr₂)_q, resembling the structure of liquid phase is used, and a set of reasonable thermodynamic parameters, which are in self-consistence and also in compatibility with the other lanthanide halide and alkali halide mixture systems, are obtained with the phase diagram and thermodynamic properties data accounted for satisfactorily. The compounds K₂EuBr₄ and KEu₂Br₅ are confirmed to melt congruently at 828 K and 878 K, respectively. The compound KEuBr₃ is detected to peritectically decompose at 831 K, which is about 15 K lower than the reported experimental data. The present work suggests the more considerable investigations on the stability of the compounds.

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