Modeling of the Thermodynamics of the Pseudobinary RbCl-$GdCl_3$ System

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The Gibbs energies of formation of the pseudobinary compounds Rb_3GdCl_6(s) and $RbGd_2Cl_7$(s) from the constituent metal halides, determined by Knudsen effusion mass spectrometry, were compared with the thermodynamic properties of the solid and liquid phases of the RbCl-$GdCl_3$ system, obtained by different methods. The compatibility of the results obtained in this work for pseudobinary compounds with literature data was assessed by an optimization procedure using the CALPHAD method. The liquid phase in the RbCl-$GdCl_3$ system was described by the associate model. The phase diagram, thermodynamic functions of mixing of the system studied, and the Gibbs energies of formation of the pseudobinary compounds: Rb_2GdCl_5(s), Rb_3GdCl_6(s), and $RbGd_2Cl_7$(s) resulted from this optimization procedure.

Key words: Coupled Phase Diagram; Rubidium Chloride-Gadolinium Chloride System; Thermodynamic Functions of Mixing; Thermodynamic Properties.

1. Introduction

The thermodynamic properties of the pseudobinary system RbCl-$GdCl_3$ have in the last few decades been determined by different methods. The phase diagram of this system has been measured by Seifert et al. [1] by differential thermal analysis. The phase diagram of the system RbCl-$GdCl_3$ is characterized by three eutectics and three compounds in the solid phase: Rb_2GdCl_5(s), Rb_3GdCl_6(s), and $RbGd_2Cl_7$(s). Two of them: Rb_3GdCl_6(s) and $RbGd_2Cl_7$(s) are stable at high temperatures and melt congruently; they exist as: low (L) and high temperature (H) modifications. Rb_2GdCl_5(s) is stable at ambient temperature and decomposes in the solid phase without formation of a liquid. The enthalpies of formation of Rb_2GdCl_5(s), L-Rb_3GdCl_6(s), and L-$RbGd_2Cl_7$(s) have been determined by solution calorimetry and e.m.f. measurements by Seifert et al. [1, 2]. The enthalpy of mixing in the liquid RbCl-$GdCl_3$ system in the whole composition range has been studied calorimetrically at 1263 K by Dienstbach and Blachnik [3]. Recently, Ma et al. [4] carried out an optimization of the RbCl-$GdCl_3$ system, using the CALPHAD technique.

The present work is a continuation of our systematic study of the thermodynamics of the ACl-$LnCl_3$ systems (A = Rb, Cs; Ln = Ce, Pr, Nd, Gd) [5 – 9]. The Gibbs energies of formation of H-Rb_3GdCl_6(s) and L-$RbGd_2Cl_7$(s) from the constituent metal halides have been previously determined by us from a vaporization study performed by means of Knudsen effusion mass spectrometry (KEMS) [8]. Combination of the Gibbs energies obtained with the calorimetric data [1] yielded the entropies of formation of these compounds [8].

The aim of the present work was to study the compatibility of thermodynamic functions of formation of the H-Rb_3GdCl_6(s) and L-$RbGd_2Cl_7$(s) phases obtained by vaporization studies with thermodynamic data available in the literature for the system studied. In addition, the entropy of mixing of the liquid phase should result from this study.

2. Phase Diagram Calculations

The experimental phase diagram [1], the thermodynamic functions of solid phases [1, 8] (see Table 1) and the enthalpy of mixing of the liquid phase, digital-

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Table 1. Thermodynamic functions of formation of pseudobinary compounds from the constituent metal halides in the RbCl-GdCl$_3$ system (at temperature T or temperature range) collected from literature and obtained from an optimization procedure.

Compound	T (K)	$\Delta_f G^o(T) = a + bT$ (J mol^{-1})		Method	Ref.
		a	b		
L-Rb$_3$GdCl$_6$	298 – 680	−49829	−36.1	Optimization	This work
	298	−52000	—	Calorimetry	[1]
	573	−46600	−36.0	E.m.f.	[1]
H-Rb$_3$GdCl$_6$	680 – 1107	−45071	−43.1	Optimization	This work
	800	−43600^a	−39.4^b	KEMS	[8]
Rb$_3$GdCl$_6$	1112.5	−51000^c	−59.3^c	Optimization	[4]
Rb$_2$GdCl$_5$	298 – 673	−58067	6.0	Optimization	This work
	298	−53700	—	Calorimetry	[1]
	573	−53400	6.1	E.m.f.	[1]
L-RbGd$_2$Cl$_7$	298 – 850	−30927	−25.14	Optimization	This work
	298	−32800	—	Calorimetry	[1]
	573	—	−1.2^d	E.m.f.	[2]
	800	—	−9.8^b	KEMS	[8]
H-RbGd$_2$Cl$_7$	850 – 893	−19397	−38.7	Optimization	This work
RbGd$_2$Cl$_7$	904	−31800^c	−42.67^c	Optimization	[4]

[a] Enthalpy of formation of H-Rb$_3$GdCl$_6$(s) recalculated from the enthalpy of formation of L-Rb$_3$GdCl$_6$(s) [1] using an estimated enthalpy of the phase transition L → H [8] (see Section 2).

[b] Entropies of formation calculated from calorimetric enthalpies of formation [1] and Gibbs energies of formation of respective compounds obtained by vaporization studies [8].

[c] Values given without explanation to what temperature modification they relate [4].

[d] Entropy of formation calculated from calorimetric enthalpy of formation [2] and e.m.f. Gibbs energy measured at 573 K.

Table 2. Coefficients of (1), describing the Gibbs energy of mixing in the liquid RbCl-GdCl$_3$ system obtained from the optimization procedure.

	A_1 J mol^{-1}	B_1 J mol^{-1} K^{-1}	A_2 J mol^{-1}	A_3 J mol^{-1}	A_4 J mol^{-1}
RbCl-GdCl$_3$	−111323	−81.647	−57279	−45916	−65845

ized from a plot [3], were optimized by the CALPHAD method using the BINGSS program [10]. The data for solid and liquid RbCl(s, l) and GdCl$_3$(s, l), used in the calculations, were taken from the IVTANTHERMO database [11] and from [12], respectively. The calorimetric enthalpy of formation of L-Rb$_3$GdCl$_6$(s) [1] was recalculated up to the temperature range of vaporization experiments including our estimated enthalpy of the phase transition L → H for Rb$_3$GdCl$_6$(s) [8] (see Table 1). The dependences of the enthalpies and entropies of formation on temperature have been neglected (Neuman-Kopp rule). Moreover, the calculation of the entropy of formation of H-Rb$_3$GdCl$_6$(s) had to be revised (see Table 1) because of an incorrect calorimetric value of the enthalpy of formation of L-Rb$_3$GdCl$_6$(s) given in [2] (used in earlier calculations), which therefore slightly differs from the original paper [8].

The liquid phase of the RbCl-GdCl$_3$ system was described by the association model with one associate A$_p$B$_q$ [13]. The other accessible models in the BINGSS program [10] have not been compatible with the measured phase diagram.

The best fitting was found with a four-coefficient polynomial. The entropy of mixing in the fitted model has been described by the one-parameter polynomial [13]

$$
\begin{aligned}
& G(T) - H^{\mathrm{SER}} = \\
& RT\{x_1 \ln(x_1) + x_2 \ln(x_2) + x_\mathrm{a} \ln(x_\mathrm{a}) - n \ln(n)\} \qquad (1) \\
& + (A_1 + B_1 T)x_\mathrm{a} + (A_2 x_1 x_2 + A_3 x_1 x_\mathrm{a} + A_4 x_2 X_\mathrm{a})/n,
\end{aligned}
$$

where x_1 and x_2 are the number of moles of the system components in one mole of liquid mixture, x_a is the number of moles of associate in one mole of liquid mixture, and $n = x_1 + x_2 + x_\mathrm{a}$.

The parameters of enthalpy and entropy of mixing in the liquid RbCl-GdCl$_3$ system, obtained in the optimization procedure, are given in Table 2.

3. Results and Discussion

The coupled phase diagram of the RbCl-GdCl$_3$ system is presented in Figure 1. Generally, the calculated phase diagram agrees with that measured by Seifert et al. [1]. Small differences between the measured and calculated phase diagrams are observed for the melting temperatures of the compounds and the eutectic

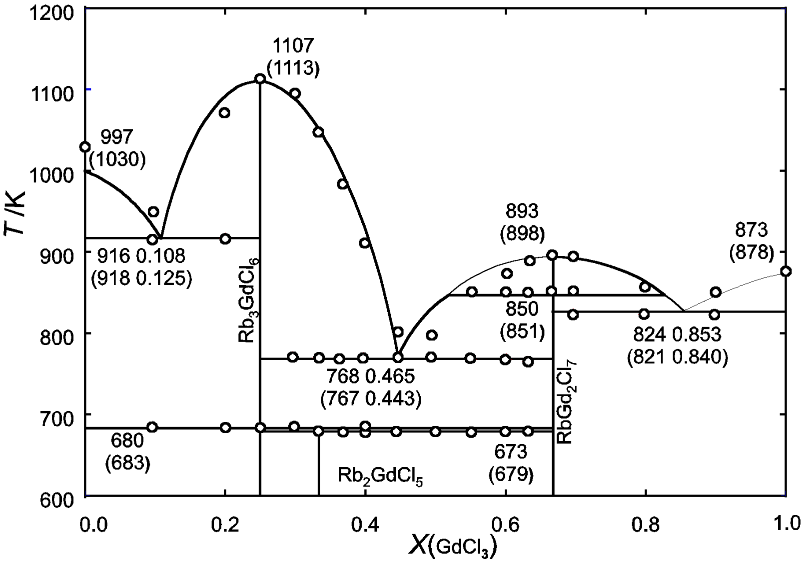

Fig. 1. Measured [1] (points and values given in parentheses) and calculated (lines and values given without parenthesis) phase diagram of the RbCl-GdCl3 system.

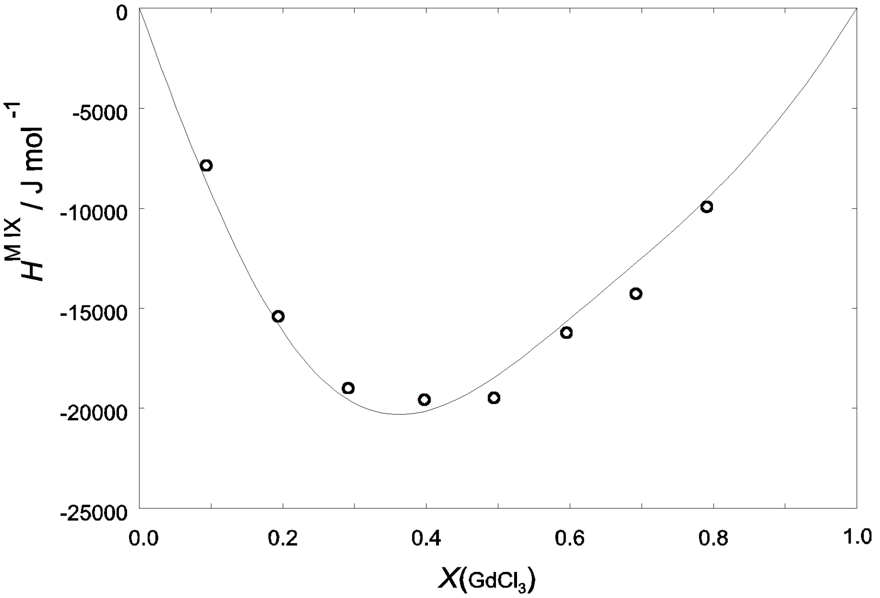

Fig. 2. Measured [3] (circles) and calculated (line) enthalpy of mixing of the RbCl-GdCl3 system.

parameters (temperature, chemical composition of the melt). The calculated temperatures of melting of the compounds in the analyzed system differ from the measured ones by up to 5.5 K, whereas in case of RbCl(s) a big difference up to 33 K, is observed (see Fig. 1).

The liquid phase of pseudobinary systems ACl-LnCl$_3$ (A = alkali metal; Ln = lanthanide) have been described, successfully, so far, using different models. Hatem and Gaune-Escard [14] modeled the KCl-DyCl$_3$ system by a surrounded ion model. Ma et al. [4] have used a quasi-chemical model for optimization of the RbCl-GdCl$_3$ system. In this work the model with one associate [13] was selected as the most fitted one. In our modeling, in comparison with [4], the experimental enthalpy of mixing of the liquid phase [3], the L → H phase transitions for Rb$_3$GdCl$_6$(s) and RbGd$_2$Cl$_7$(s) and thermodynamic functions of formation of Rb$_2$GdCl$_5$(s) [1] were taken additionally into consideration.

The enthalpy of mixing and entropy of mixing over the whole composition range of RbCl-GdCl$_3$ obtained

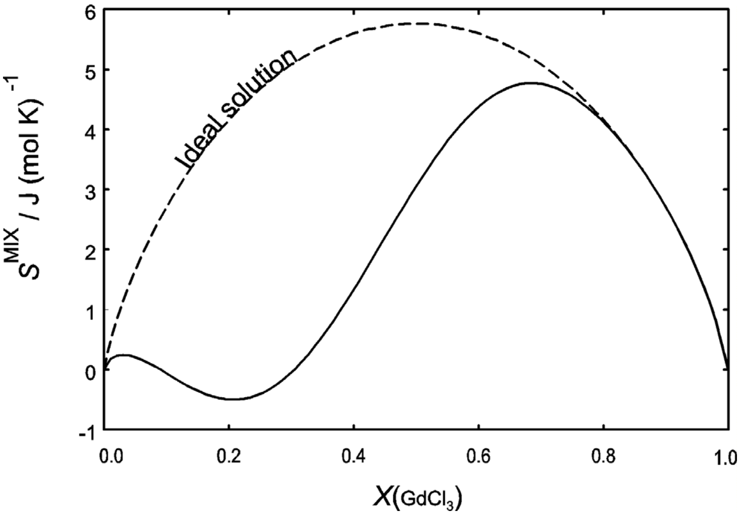

Fig. 3. Entropy of mixing of the liquid RbCl-GdCl$_3$ system obtained in the present work by thermodynamic modeling.

by thermodynamic modeling are presented in Figs. 2 and 3, respectively. The calculated enthalpy of mixing agrees well with the experimental results obtained by Dienstbach and Blachnik [3] (Fig. 2). The values of the calculated entropy of mixing are significantly smaller than the ideal entropy (Fig. 3). This indicates the strong tendency to agglomeration in the ionic liquid of the RbCl-GdCl$_3$ mixture. The minimal entropy of mixing occurs at a mole fraction of GdCl$_3$ near 0.28. It corresponds to the Rb$_3$GdCl$_6$(s) compounds, and this may result from a local order associated with extensive complex formation in the strongly interacting RbCl-GdCl$_3$ mixture. It is consistent with the presence of complex configurations such as $[\mathrm{GdCl}_6]^{3-}$ in the liquid phase of this system [3]. It is also consistent with the results obtained for similar systems of the type ACl-LnCl$_3$ (A = alkali metal; Ln = lanthanide) [e. g. 15, 16]. The stoichiometry of the liquid associate, obtained by the optimization procedure, equals 2.45 : 1, a non-integer number. We assume that this may result from a small amount of another associate of different stoichiometry. This may be connected with the existence in the solid phase of the investigated system of two congruently melting compounds (see Fig. 1). The possibility of the presence of other associates (e. g. stoichiometry 1 : 1) cannot be excluded, we think of [5]. The negative value of the coefficient B_1 in (1) shows the probable presence of a positive non-configurational contribution to the entropy of mixing.

The enthalpies and entropies of formation of the (L, H)-Rb$_3$GdCl$_6$(s), Rb$_2$GdCl$_5$(s) and (L, H)-RbGd$_2$Cl$_7$(s) compounds obtained in the present work are presented in Table 1. The enthalpies of formation of Rb$_3$GdCl$_6$(s), Rb$_2$GdCl$_5$(s) and L-RbGd$_2$Cl$_7$(s), calculated in this work agree well with the experimental data. A complete description of the formation reaction of H-RbGd$_2$Cl$_7$(s) has been obtained in this work for the first time. The entropy of formation of L-Rb$_3$GdCl$_6$(s) calculated in this work agrees well with e.m.f. data, whereas it differs significantly from the value optimized by Ma et al. [4]. For H-Rb$_3$GdCl$_6$(s) and Rb$_2$GdCl$_5$(s) the entropies obtained in this work agree with data from KEMS and e.m.f., respectively. The entropies of formation of L-RbGd$_2$Cl$_7$(s) obtained by different methods are quite different. In this case it is difficult to select a more accurate result.

The slight differences observed between calculated and measured temperatures of melting for Rb$_3$GdCl$_6$(s) and RbGd$_2$Cl$_7$(s) (see Fig. 1) probably result from a simplified liquid phase model used in the optimization procedure, assuming the existence of one associate only.

4. Conclusions

The assessment of the results obtained for pseudobinary compounds by Knudsen effusion mass spectrometry and other literature data has been made by computer modeling. The phase diagram, enthalpy of mixing and entropy of mixing of liquid mixtures of the system studied have been obtained by the optimization procedure. Compatibility between the phase diagrams and the thermodynamic functions of formation for pseudobinary compounds determined in the present study was found. The entropies of mixing of liquid phases of RbCl-GdCl$_3$ obtained in the present work show the possibility of the presence of more than one associate in the liquid phase.

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[1] H. J. Seifert, J. Sandrock, and G. Thiel, Z. Anorg. Allg. Chem. **598/599**, 307 (1991).

[2] H.J. Seifert, J. Therm. Anal. Calorim. **67**, 798 (2002).

[3] F. Dienstbach and R. Blachnik, Z. Anorg. Allg. Chem. **412**, 97 (1975).

[4] Z. Ma, Y. Sun, Y. Ding, Y. Wang, Z. Qiao, and X. Ye, CALPHAD **30**, 88 (2006).

[5] I. Lisek, J. Kapała, and M. Miller, J. Alloys Comp. **278**, 113 (1998).

[6] I. Lisek, J. Kapała, and M. Miller, J. Alloys Comp. **280**, 77 (1998).

[7] I. Rutkowska, J. Kapała, and M. Miller, Polska Metalurgia w latach 1998-2002, Wydawnictwo Naukowe „AKAPIT“, Kraków 2002, Vol. 1, p. 39.

[8] I. Rutkowska, K. Hilpert, and M. Miller, Z. Anorg. Allg. Chem. **630**, 1116 (2004).

[9] J. Kapała and I. Rutkowska, CALPHAD **28**, 275 (2004).

[10] H. L. Lukas, Computer Programs BINGSS, BINFKT, Max-Planck-Institut für Metallforschung, Heisenbergstr. 5, D-70569 Stuttgart, Germany.

[11] L. V. Gurvich, V. S. Yungman, G. A. Bergman, I. V. Veitz, A. V. Gusarov, V. S. Iorish, V. Ya. Leonidov, and V. A. Medvedev, IVTANTHERMO – Thermodynamic Properties of Individual Substances, Glushko Thermocenter of RAS 2000.

[12] L. Rycerz, Thermochemistry of lanthanide halides and compounds formed in lanthanide halide-alkali metal halide systems, Scientific Papers of the Institute of Inorganic Chemistry and Pure Elements of the Wrocław University of Technology No. 68, Mon. No. 35, 2004, (in Polish).

[13] F. Sommer, Z. Metallkd. **73**, 72 (1982).

[14] G. Hatem and M. Gaune-Escard, Thermochim. Acta **293**, 137 (1997).

[15] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, Thermochim. Acta **236**, 67 (1994).

[16] G. N. Papatheodorou and O. J. Kleppa, J. Phys. Chem. **78**, 178 (1974).